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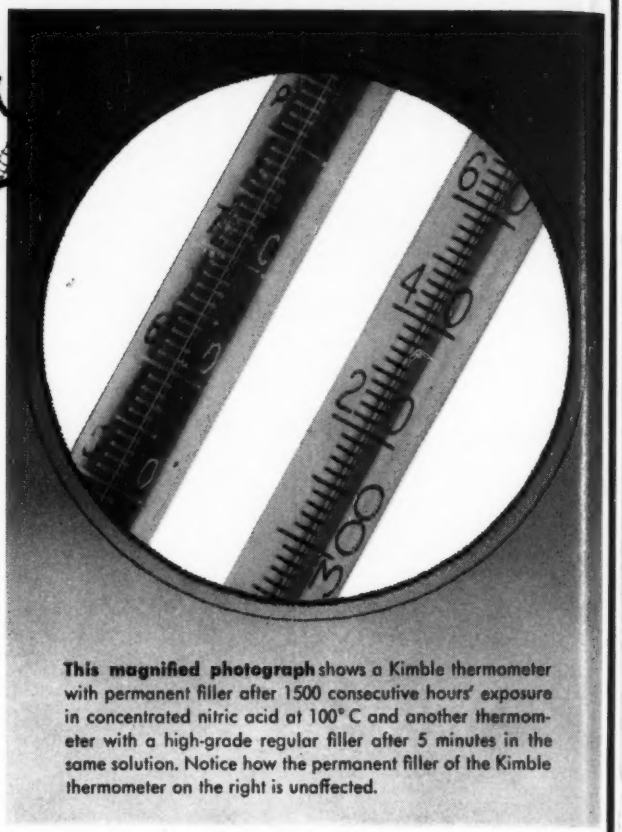

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JOURNAL OF CHEMICAL EDUCATION

Amphoteric Molecules, Ions, and Salts, *David Davidson* 550

A Chemistry Course Including Both Qualitative and Quantitative Analysis, *Bruce McDuffie* 560

What a Chemistry Teacher Should Know About Oil, *Howard C. Anderson* 563

Friedlieb Ferdinand Runge: A Forgotten Chemist of the Nineteenth Century, *Berthold Anft* 566

A Roult's Law Experiment for the General Chemistry Course: Manometry Without a Manometer, *Frank E. Harris and Leonard K. Nash* 575

Calorimeter for Determining Heat Capacities of Liquids, *Stanley A. Greene* 577

The Uses of the Ultracentrifuge, *J. W. Williams* 579

The Intrasemester One-hour Examination, *J. B. Ramsey* 585

A Micro Air-flow Reaction Apparatus, *John T. Stock and M. A. Fill* 586

A Laboratory Demonstration of Blood Catalase, *R. Quentin Blackwell and Leonard S. Fosdick* 588

A Variable Periodic System, *Roderich Scheer* 590

Time-saving Reading in Chemistry, *A. J. Pellettieri* 591

Report of the New England Association of Chemistry Teachers
The Historical Approach to Chemical Concepts, *Samuel Madras* 593

Editor's Outlook 549

Out of the Editor's Basket 33

Letters to the Editor 598

Recent Books 600

Frontispiece—Friedlieb Ferdinand Runge 25

Advertisers' Index 45

Tested Demonstrations in General Chemistry 19

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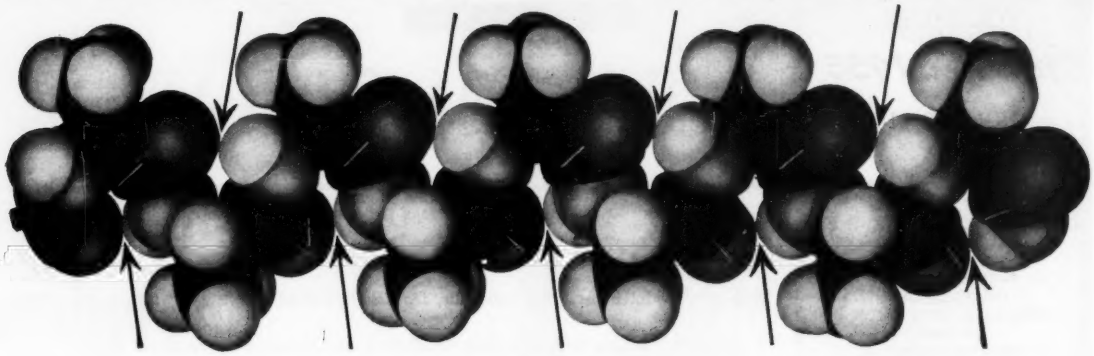
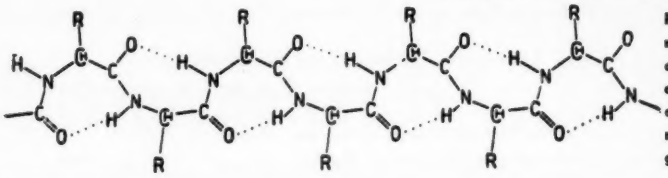


MACRO-MOLECULES



Photograph shows how atom models are combined to construct macro-molecules. Formula is for 2_{7b}-folding of polypeptide chain. Side-chains are indicated by methyl groups forming an alanine chain. Note the clear periodicity. Hydrogen-bridge connections with hooks (shown by arrows) possess sufficient mobility for construction and hold the finished chain tightly together. Conversion to the 2_{7a}-folding and flapping over are easy.

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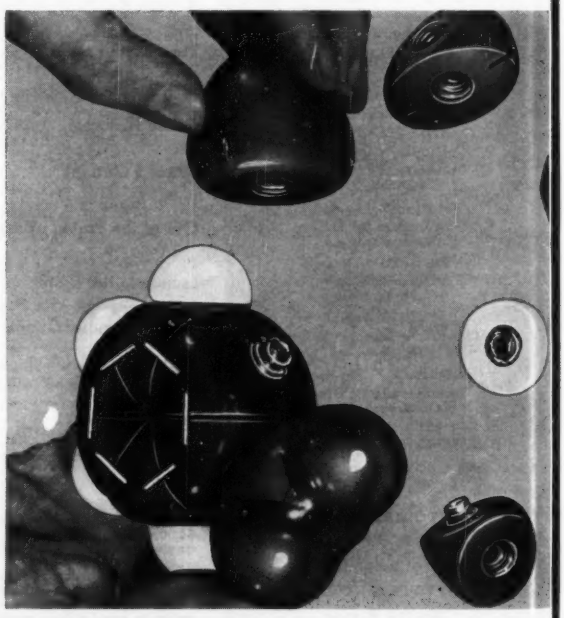

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11. METALLURGY

A. ORES AND MINERALS

11-1 Gold foil, large lump Na, sodium press, foils and wires of various metals, electric bell and battery with leads. **Show conductivity, malleability, ductility.**

11-2 **Exhibit:** native, oxide, carbonate, sulfide, chloride, and sulfate ores.

B. CONCENTRATION OF ORE

*11-3 *Panning.* Gold-bearing ore with excess of mud in prospector's pan. **Show panning process.**

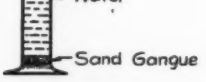
Flotation phenomena

*11-4 *Selective adsorption.* Activated charcoal in 25 mm. × 30 cm. tubing clamped vertically; methylene blue solution, two 400 ml. beakers, white and brown sugar. **Pour blue solution through column, illustrating adsorption. Tube may be used repeatedly for years. Mention brown sugar decolorization.**

11-5 Tube of methylene blue solution; another of methylene blue solution plus kaolin. **Show how methylene blue has been adsorbed.**

*11-6 A dozen dots (from paper punch) of paper which is white on one side, black on other, thrown into a 250 ml. Erlenmeyer flask containing 50 ml. CCl_4 + 50 ml. water. A dozen dots into a similar flask containing 50 ml. benzene + 50 ml. water. **Show black faces toward organic solvent; selective adsorption.**

*11-7 *Flotation.* See Figure 11-7. Mineral oil, finely powdered Pb_3O_4, clean sand, 100 ml. cylinder. **Shake equal volumes of water and oil with sand + Pb_3O_4: shows flotation of lead ore.**



FLOTATION

Figure 11-7

11-8 *Magnetic separation.* Fe_3O_4, sand, paper, magnet. **Show magnetic separation, as for magnetite.**

C. REDUCTION OF THE ORE

11-9 Mixture 2 g. CuO + 5 g. powdered charcoal in tube over burner, with delivery tube leading into tube of limewater; 15 cm. evaporating dish. **Heat mixture of CuO + C, showing CO_2 and Cu formed, using water to wash away excess charcoal in evaporating dish.**

11-10 See thermit reaction, experiment 7-3.

*11-11 $ZnCO_3$ in tube over burner, with delivery tubing leading into tube of limewater. **Heat. Show CO_2 is evolved, ZnO forms.**

11-12 Tank O_2 leading to 15 mm. × 30 cm. horizontal tube over wing-tip burner, exit tube into very dilute $KMnO_4$-aq.; porcelain boat containing ZnS. **Insert porcelain boat of ZnS; heat contents in stream of oyxgen. SO_2 evolves, decolorizing the $KMnO_4$; ZnO forms.**

*11-13 Steel wool, 600 ml. beaker half-full of $CuSO_4$-aq. **Immerse steel wool, show displacement of the Cu^{++}, forming $FeSO_4 + Cu$.**

D. REFINING THE METAL

*11-14 Mud, $CuSO_4$-aq., apparatus for electroplating. **Show copper is plated out of muddy solution.**

*Footnotes

11-3 A humorous twist is to cement a gold-foiled chocolate candy to the bottom of the pan; conceal with muddy water. Go through the process of panning and washing off the supernatant muddy water; finally, the imitation gold coin flashes into view.

11-4 This and 11-5 and 11-6 illustrate selective adsorption, and prelude 11-7 which involves the principle of this selective "wetting" of ore (which floats in the oil) and the gangue (silicates, which sink in the water).

11-6 This makes a better display for the laboratory period, rather than a demonstration from the lecture desk.

11-7 An elegant experiment; be sure to use the proper grades of sand and Pb_3O_4.

11-11 Show the class that the ZnO formed in this experiment, and in 11-12, is yellow when hot, then turns white upon cooling.

11-13 This process is used for recovering the last quantities of Cu from thoroughly worked copper mines. Scrap iron is dumped into mile-long canals through which the dilute cupric sulfate solution flows. Copper slime sinks to the bottom; the $FeSO_4$ byproduct is also sold.

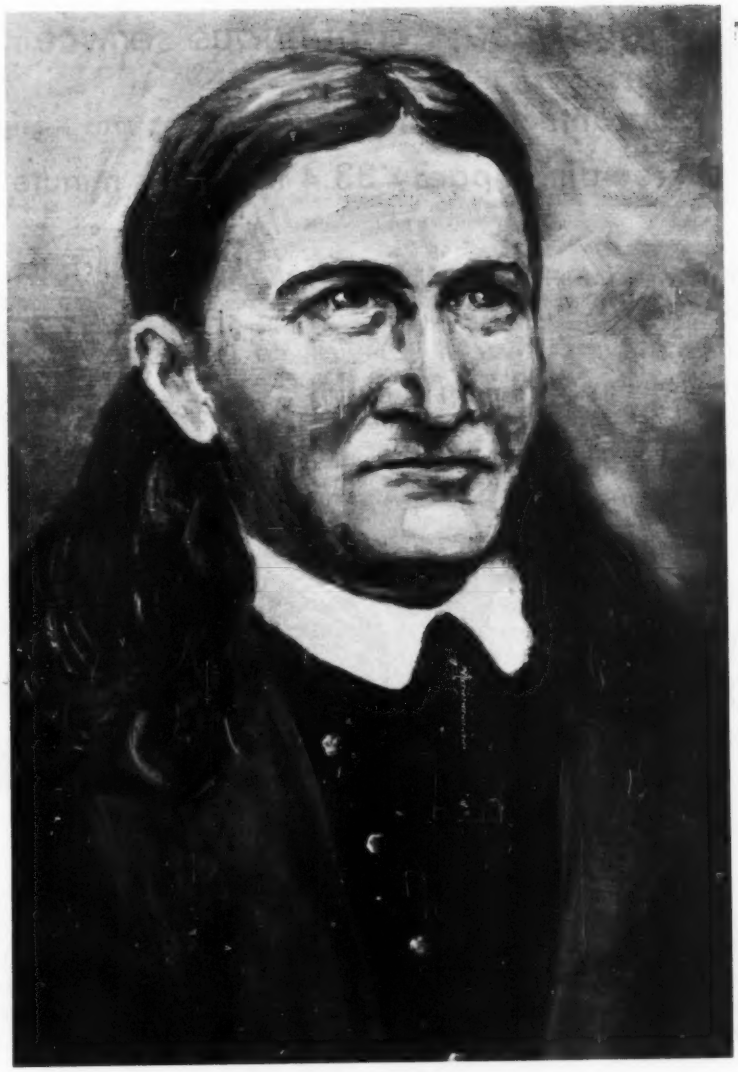
11-14 This standard piece of equipment will find frequent use. It consists of two large electrodes with a lamp in series which lights up whenever the D.C. current is flowing; 40 volts is usually sufficient. Reverse the polarity to show how copper always plates out on the negative pole. Or use apparatus Figure 5-6 with plate electrodes attached to the filaments.

Labels for Topic 11. (For code, see instructions for assembling kits, J. Chem. Educ., **32**, 12A(1955).) 11-1-*J*-wires and foil, 11-3-*J*-gold bearing ore or candy gold pieces, 11-4-*d*-methylene blue aq., 11-4-*J*-brown sugar, 11-4-*J*-white sugar, 11-6-*w*-paper dots, black on one side, 11-6-*N*-CCl_4, 11-6-*N*-C_6H_6, 11-7-*N*-mineral oil, 11-7-*w*-Pb_3O_4, 11-7-*w*-sand, 11-8-*w*-Fe_3O_4, 11-8-*w*-sand, 11-9-*w*-CuO, 11-9-*w*-charcoal, 11-9-*N*-limewater, 11-10-*J*-thermit, 11-10-*J*-thermit, 11-10-*w*-thermit starting mixture, 11-10-*w*-granular $KClO_3$, 11-10-*w*-granulated sugar, 11-10-*d*-conc. H_2SO_4, 11-11-*w*-$ZnCO_3$, 11-11-*N*-limewater, 11-12-*d*-$KMnO_4$ aq., 11-12-*w*-ZnS, 11-13-*N*-$CuSO_4$ aq., 11-13-*J*-steel wool, 11-14-*N*-muddy water, 11-14-*N*-$CuSO_4$ aq.

Next month's Tested Demonstrations in General Chemistry

12. GROUP I. THE ALKALI METALS. THE COPPER GROUP

For a complete list of topics for 1955–6 see J. Chem. Educ., 32, 28–9(1955)



Friedlieb Ferdinand Runge

(See page 566)

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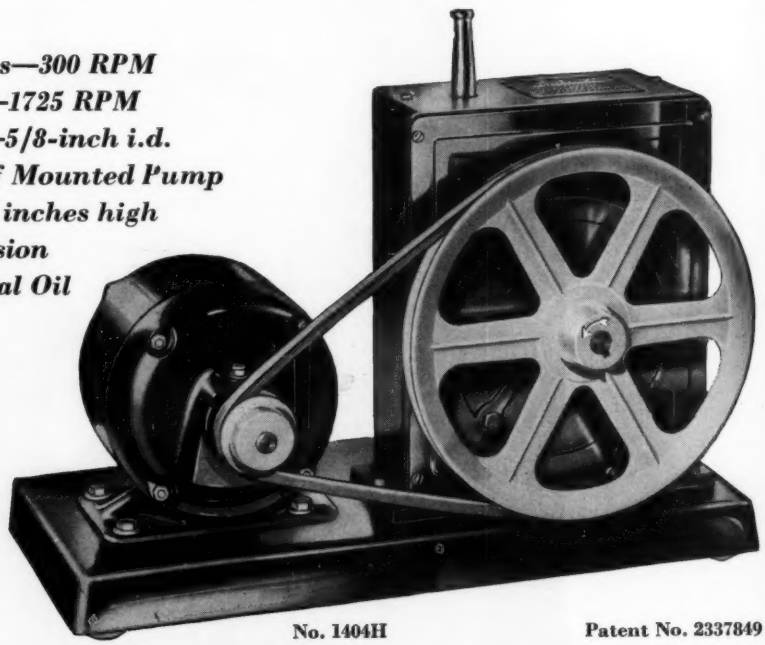

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Editor's Outlook

FIRST impressions get scoured by the passage of time. Enough of this has gone on since the Minneapolis meeting to erode some into oblivion and to reveal others as the denser substratum of conviction. Among the latter is the feeling that the professional respectability of the teaching chemist has reached a new high. Both the president of the A. C. S. and the Priestley Medalist built their addresses on themes of educational problems. The News Service breakfast speaker urged similar concerns upon the headline writers. The Division of Chemical Education was supported by the shared sponsorship of three other divisions for its symposia.

We recall with some grimness the frequency with which we used to have to listen, not so many years ago, to the old cliché: "Those who can do; those who can't teach." Unfortunately, we cannot say that adherence to this point of view is as dead as support of the phlogiston hypothesis. The gratifying aspect of our recent encounters with it has been that seldom has the academic man in the listening group had to come to his own rescue. Almost always someone successful in the research laboratory or at the administrative desk speaks from his conviction that activity in the classroom or student laboratory is of critical importance to the progress of chemistry. The transition from disinterested youth into student of science may be started by the impersonal lure of the test tube or the cyclotron, but seldom is this enough to complete the metamorphosis into a professional chemist. This requires teaching—good teaching. When the college professor does get around to pointing out that nearly all of his small graduating class will eventually enter the profession as Ph.D.'s, his status as a contributor to the advancement of science takes on a new light.

It is not our purpose here to imply that teachers have any right to think of this "new light" as including either a glow of satisfaction or the shine of a martyr's halo. Instead we would like to point out how it may embarrassingly illuminate a shortcoming in the attitude of some who do the teaching.

Much has been written, and more spoken, about the shortage of science teachers, particularly at the secondary-school level. All manner of suggestions have urged that scientifically-trained persons enter the teaching profession. We see one distressingly simple emphasis which needs to be made. *The most effective means of motivating able students to become teachers is good teaching itself.*

If the chemist in front of the classroom can feel the enthusiasm of a dual pride, both in his subject and in his position as a teacher, he has every right, in fact an obligation, to let this enthusiasm be apparent. A student who learns of chemistry only as the exalted activity involved with atom smashing, mountains of sulfur, or the maze-like piping of a catalytic cracker may well wonder why the apologetic little man in front of the room allowed himself to get there. If the student himself, even though brilliant, finds his greatest pleasure in dealing with people, he may decide early to let chemistry be the career for the genius in the next seat.

The new recruits for the teaching profession will come from those who have had the stimulation of a more satisfactory example. "Good" teaching defies definition. We shall not try. The ax we are grinding here is for the reasonableness of an enthusiasm which prompts not only a thorough understanding and appreciation of the subject but also a genuine enjoyment in seeing a mind being trained to think like a scientist. Future teachers will come from classes taught by a professor who did not act as though his presence there was an unfortunate intrusion on an otherwise productive scientific career.

Judging from the example of the greatest teachers we have known, we are not afraid that an obvious enthusiasm for his role as a teacher will leave a man satisfied with a professional life limited to the classroom. The good teacher is the first to realize that "food cannot be kept hot with the oven door open all the time." He will get his hands soiled and his mind washed clean by doing some research. His lectures will liven up; his illustrations ring true. Best of all, he will approach his job with a humility born of encounter with problems for which no answer book has been written.

If the teacher is to earn an increased respectability as a professional scientist, he must constantly remind himself of one simple fact. The two most available sources of chemical information the student has are his text and his professor. These should be distinguished from each other by observing that the latter is alive. The classes in which this is most obvious will be those from which our supply of future scientists for both the laboratory and the classroom will come.

AMPHOTERIC MOLECULES, IONS, AND SALTS

DAVID DAVIDSON
Brooklyn College, Brooklyn, New York

SUBSTANCES which function both as acids and[1] bases are said to be amphoteric or amphiprotic. For such substances the noun *ampholyte* is a convenient term. It is the aim of this paper to call attention to the splendid opportunity ampholytes afford for the teaching of acid-base principles. A simplified method of approximating the pH's of aqueous solutions of ampholytes is included.

BACKGROUND

Acids and bases are conveniently defined by means of the Brönsted equation:

$$\text{Acid}_1 \rightleftharpoons \text{Base}_1 + \text{H}^+$$

The acid and base connected by this equation are known as conjugates but the reaction is only hypothetical, since actual acid-base reactions necessarily involve the interaction of two such systems. In such reactions a proton is lost from an acid (which is thereby converted to its conjugate base) and is transferred to a base (which is thereby converted to its conjugate acid).

$$\text{Acid}_1 + \text{Base}_2 \rightleftharpoons \text{Acid}_2 + \text{Base}_1$$

The "ionization" of acetic acid, for example, involves the following proton transfer (protolysis)[2]:

$$\text{AcOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{AcO}^-$$

in which water functions as Base_2. The "hydrolysis" of sodium acetate depends upon the transfer of protons from water to acetate ion (water functions as Acid_1).

$$\text{H}_2\text{O} + \text{AcO}^- \rightleftharpoons \text{AcOH} + \text{OH}^-$$

In the acetic acid-acetate ion system the acid is uncharged and its conjugate base anionic. In a system such as ammonium ion-ammonia, on the other hand, the acid is cationic while its conjugate base is uncharged. In this second case the protolysis ("hydrolysis") of ammonium ion involves the reaction:

$$\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NH}_3$$

and the "ionization" of ammonia depends upon the reaction:

$$\text{H}_2\text{O} + \text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$$

The acidity constant K_a is a measure of the strength of an acid. It is also known as the "ionization constant" (in the case of uncharged acids) and as the "hydrolysis constant" (in the case of cationic acids). It consists of the equilibrium constant for the reaction of the acid with water, the concentration of water itself being considered constant. Thus, for the two acids mentioned above the respective K_a's are: for acetic acid,

$$K_a = \frac{[\text{H}_3\text{O}^+]\,[\text{AcO}^-]}{[\text{AcOH}]}$$

for ammonium ion,

$$K_a = \frac{[\text{H}_3\text{O}^+]\,[\text{NH}_3]}{[\text{NH}_4^+]}$$

The basicity constant K_b is a measure of the strength of a base. It is also known as the "ionization constant" (for uncharged bases) and the "hydrolysis constant" (for anionic bases). It consists of the equilibrium constant for the reaction of water with the base, the concentration of water itself being considered constant. Thus, the K_b's for the bases mentioned above are: for acetate ion,

$$K_b = \frac{[\text{AcOH}]\,[\text{OH}^-]}{[\text{AcO}^-]}$$

for ammonia,

$$K_b = \frac{[\text{NH}_4^+]\,[\text{OH}^-]}{[\text{NH}_3]}$$

For many purposes the negative logarithms of K_a's and K_b's are convenient. The corresponding symbols are pK_a and pK_b. The pK_a and pK_b of **conjugates** are interdependent. This is readily demonstrated,[3] using acetic acid as an example.

Process	*Constant*
$\text{AcOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{AcO}^-$	K_{a_1}
$\text{H}_2\text{O} + \text{AcO}^- \rightleftharpoons \text{AcOH} + \text{OH}^-$	K_{b_1}

adding:

$$2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \qquad K_{a_1}K_{b_1}$$

therefore:

$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_{a_1}K_{b_1}$$

but:

$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_w = 10^{-14} \text{ at } 25°$$

hence:

$$pK_{a_1} + pK_{b_1} = 14$$

Since the sum of the pK_a and pK_b for **conjugates** is 14, one constant is readily calculated from the other. It also follows from this relationship that *an acid and*

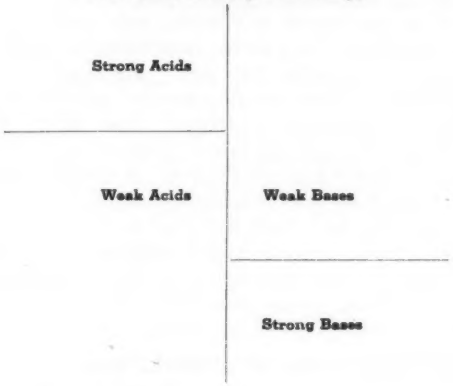
[1] Some dictionaries use *or* rather than *and*. *Or* fails to imply that these substances function simultaneously as acids and bases.

[2] In this article, the acid-base equations are written in conformity with the previous equation; that is, one set of conjugates flanks the arrows while the other appears at the extreme left and right.

[3] DAVIDSON, D., AND K. GELLER, J. CHEM. EDUC., **30**, 238 (1953).

its conjugate base can be equal in strength only when $pK_a = pK_b = 7$. The value seven is therefore a natural origin from which to set out to designate acid and base strengths. If $pK_a < 7$, then $pK_b > 7$, and vice versa. By choosing two more points, 2 and 12, the system of strength classification given in Table 1 is obtained.[4] The tetrachotomy—strong, intermediate, weak, and feeble—serves to implement the mathematical relationship: $pK_a + pK_b = 14$. Attempts to express the strength relationships of conjugates in terms of the traditional dichotomy—strong and weak—have only led to inadequate or misleading statements.[5] The difficulty is due to the fact that, in the dichotomy, weak acids have strong or weak conjugates, depending on how weak the acid is. The same is true for the conjugates of weak bases (see the diagram).

Acid-Base Scale (Dichotomy)



AMPHOLYTES IN GENERAL

As has been said above, the loss of a proton from a monoprotic acid yields a base. The removal of *one* proton from a *diprotic* acid, however, yields an ampholyte, since this product of protolysis is not only the conjugate base of the original diprotic acid but also the conjugate acid of the diprotic base which it yields on releasing the second proton. The process may be reversed by starting with a diprotic base and adding two protons in succession. Such simple ampholytes are, therefore, in equilibrium with their conjugate diprotic acids and diprotic bases as indicated below.

$$\text{Diprotic acid} \rightleftharpoons H^+ + \text{Ampholyte}$$
$$\text{Ampholyte} \rightleftharpoons H^+ + \text{Diprotic base}$$

It will be found convenient to tabulate the species in these simultaneous equilibria and to examine them from the standpoint of their dominant constants (Table 2). The diprotic acid is dominated by the first acidity constant, K_{a_1}. Normally this is larger than K_{a_2}. In a symmetrical diprotic acid statistical considerations[6] require that K_{a_1} be at least four times K_{a_2}. Usually this ratio is much larger owing to electrostatic influences.[7] Since $\log 4 = 0.60$, pK_{a_2} *exceeds* pK_{a_1} by at least 0.60. (The inverted order of the pK_a's arises, of course, from their being *negative* logarithms.)

The basicity constant of a simple ampholyte stems from the conjugate of the acidic group responsible for pK_{a_1} in the diprotic acid. Since pK_{a_1} and pK_{b_1} refer to conjugates their sum is 14. Since, furthermore, pK_{a_2} is larger than pK_{a_1} by at least 0.6, it follows that:

$$pK_{a_2} + pK_{b_1} \gtrless 14.60$$

This is the fundamental relationship which exists between the (nonconjugate) acidity and basicity constants of ampholytes.

The inventory of species discussed above may often be useful in appraising the character of the several species involved in a polyprotic acid-base system. For example, given the two pK_a's of the carbonic acid system (Table 3), the remainder of the constants may be obtained by following the rule: $pK_{a_1} + pK_{b_1} = 14$. Thus, the species H_2CO_3 is characterized by pK_{a_1} (6.5); the first protolysis product, HCO_3^-, is an am-

TABLE 1
Strength Classification of Acids and Bases (Tetrachotomy)

Strength designation of conjugate acid	*Acidity scale* pK_a	pK_b	*Strength designation of conjugate base*
Strong (A_s)			Feeble (B_f)
	2	12	
Intermediate (A_i)			Weak (B_w)
	7	7	
Weak (A_w)			Intermediate (B_i)
	12	2	
Feeble (A_f)			Strong (B_s)

TABLE 2
Species Inventory for Diprotic Acid-Base Systems

Species[a] *Type 1*	*Type 2*	*Type 3*	*Dominant constants—Acidity*	*Basicity*	*Character*
H_2X	H_2Y^+	H_2Z^{++}	pK_{a_1}	...	Diprotic acid
HX^-	HY	HZ^+	pK_{a_2}	pK_{b_1}	Ampholyte
X^{--}	Y^-	Z	...	pK_{b_2}	Diprotic base

[a] H_2X is exemplified by succinic acid, H_2Y^+, by the cation in *p*-aminobenzoic acid hydrochloride or glycine hydrochloride H_2Z^{++}, by the cation in ethylenediamine dihydrochloride.

[4] An earlier version of this classification scheme was given by DAVIDSON, D., J. CHEM. EDUC., **19**, 154 (1942).

[5] Some examples of such statements are:
(*a*) GLASSTONE, S., "Textbook of Physical Chemistry," 2nd ed., D. Van Nostrand Co., Inc., New York, **1946**, p. 984: "If the acid HA is weak, the conjugate base A^- will be fairly strong, and interaction with the solvent, acting as an acid, will take place to a definite extent."
(*b*) WHELAND, G. W., "Advanced Organic Chemistry," 2nd ed., John Wiley & Sons, Inc., New York, **1949**, p. 76: "...a weak acid...must have a *strong conjugate* base."

[6] GREENSPAN, J., *Chem. Revs.*, **12**, 339 (1933). In brief, the argument may be given as follows: A symmetrical diprotic acid has twice as many opportunities for losing one proton as does either acidic group alone; likewise, the diprotic base has twice as many opportunities for accepting a proton as does either basic group alone. Hence, the first protolysis constant differs from the second by a factor of $2 \times 2 = 4$.

[7] WHELAND, G. W., "Advanced Organic Chemistry," 2nd ed., John Wiley & Sons, Inc., New York, **1949**, Chap. 11.

TABLE 3
Species Inventory for the Carbonic Acid System

Species	Dominant constants pK_a's	Dominant constants pK_b's	Character
H_2CO_3	(1) 6.5	...	Diprotic acid
HCO_3^-	(2) 10.7	(1) 7.5	Ampholyte
CO_3^{--}	...	(2) 3.3	Diprotic base

pholyte, characterized by pK_{a_2} (10.7) and pK_{b_1} (14 − 6.5 = 7.5); the second protolysis product, CO_3^{--}, is a diprotic base characterized by pK_{b_2} (14 − 10.7 = 3.3). The ampholyte, bicarbonate ion, is thus seen to be a weak base and a weak acid, its basicity being about a thousandfold stronger than its acidity.

TABLE 4
Species Inventory for the Phosphoric Acid System

Species	Dominant constants pK_a's	Dominant constants pK_b's	Character
H_3PO_4	(1) 2.0	...	Triprotic acid
$H_2PO_4^-$	(2) 7.2	(1) 12.0	Acidic ampholyte
HPO_4^{--}	(3) 12.4	(2) 6.8	Basic ampholyte
PO_4^{-3}	...	(3) 1.6	Triprotic base

In the case of phosphoric acid (Table 4), two ampholytes occur between the triprotic acid and the triprotic base, one being preponderantly acidic and the other preponderantly basic. Note again that the pK_a of one species plus the pK_b of the next lower species totals 14, while the pK_a plus the pK_b of the amphoteric species exceeds 14 by a considerable amount.

TABLE 5
Species Inventory for the Water System

Species	Dominant constants pK_a's	Dominant constants pK_b's	Character
H_3O^+	(1) −1.7	...	Diprotic acid
H_2O	(2) 15.7	(1) 15.7	Ampholyte
OH^-	...	(2) −1.7	Diprotic base

The system, water, is of interest (Table 5). The reactions and expressions involved are:

$$H_3O^+ + H_2O \rightleftharpoons H_3O^+ + H_2O \qquad (1)$$

$$K_{a_1} = \frac{[H_3O^+]\,[H_2O]}{[H_3O^+]} = [H_2O]$$

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- \qquad (2)$$

$$K_{a_2} = \frac{[H_3O^+]\,[OH^-]}{[H_2O]} = \frac{K_w}{[H_2O]}$$

TABLE 6
Strength Types of Ampholytes (Restricted)

Diprotic acid[a]	Ampholyte	Diprotic base[a]
A_iA_i	B_wA_i	B_wB_w
A_iA_w	B_wA_w	B_wB_i
A_wA_w	B_iA_w	B_iB_i

[a] Feeble acids and bases have been omitted; consequently their conjugates, strong bases and acids, also fail to appear.

In conformity with the K_a's given above for acetic acid and ammonium ion, the concentration of water (as *a base* in (1) and as an acid in (2)) on the left side of the chemical equations is included in the constant.

STRENGTH TYPES OF AMPHOLYTES

It is apparent that the species H_2O is both a feeble base and a feeble acid. If other acids or bases are to manifest themselves at low concentrations in water, their pK_a's or pK_b's must be sufficiently below 15.7 to compensate for their relatively low concentrations. For example, to be merely as effective as water itself in producing hydronium ions, an acid of pK_a 12 would be required in a concentration of 0.01 *M*. Hence, the justification for considering a pK_a of 12 the borderline between weak and feeble acids. In qualitative organic analysis, feeble acids and bases are generally considered nonacidic and nonbasic, respectively.[8]

From the relationship $pK_{a_2} + pK_{b_1} \lesseqgtr 14.6$, it follows that if an ampholyte is a strong acid ($pK_{a_1} < 2$) it must necessarily be a feeble base ($pK_{b_1} > 12.6$). If, as may be desirable for many practical purposes, *feeble* acids and bases are disregarded, ampholytes may be limited to the three strength types B_wA_i, B_wA_w, and B_iA_w. The relationship of these to their diprotic acids and bases is given in Table 6. A stable ampholyte of the type B_iA_i is impossible because, if, for example, pK_{a_2} and pK_{b_1} were both five their sum would not be $\lesseqgtr 14.6$. Such a system would undergo a spontaneous protolysis in aqueous solution to form a tautomer of the type B_wA_w, both constants then being nine. γ-Aminobutyric acid is an example of such a case.

STRUCTURAL TYPES OF AMPHOLYTES

It has been demonstrated above that simple, *anionic* ampholytes are derived from uncharged, diprotic acids. Among organic examples, the two acidic groups may be identical in structure or different. This opens the way for a large variety of structural types in which the acidic groups may be any of those given in Table 7. *Uncharged* or molecular ampholytes may contain one of each of the acidic and basic groups in Table 7, provided, as was indicated in the previous section, at least one group is *not* intermediate in strength. Simple, *cationic* ampholytes are derived from uncharged, diprotic bases. In *dipolar ionic* ampholytes, the acidic group is the cationic conjugate of one of the uncharged, basic groups in Table 7, and the basic group is the anionic conjugate of one of the uncharged, acidic groups in the table.

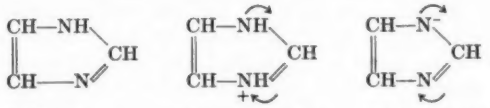
Some examples of *anionic* ampholytes are found in potassium acid phthalate, sodium barbiturate, and sodium thioglycolate; of predominantly *uncharged* ampholytes in sulfanilamide, adrenalin, 8-hydroxyquinoline, *p*-aminophenol, and anthranilic acid; of predominantly *dipolar ionic* ampholytes in glycine and ε-aminocaproic acid; of *cationic* ampholytes in procaine and *p*-phenylenediamine monohydrochloride. An interesting case of an ampholyte is found in im-

[8] DAVIDSON, D., J. CHEM. EDUC., **19**, 221 (1942).

TABLE 7
Uncharged Groups Available for Ampholytes

Acidic groups		Basic groups	
Weak	*Intermediate*	*Weak*	*Intermediate*
Hydroxyl (phenols, enols of β-diketones, etc.)	Hydroxyl (enols of cyclic β-diketones, etc.)	Amino (aromatic)	Amino (aliphatic)
Oximino	Sulfhydryl (thiophenols)	Hydrazino (aromatic)	Hydrazino (aliphatic)
Imido	Carboxyl	Azomethino (RCH=NR')	Amidino
1° or 2° nitro			Guanidino (aromatic)
Sulfhydryl (mercaptans or thioamides)			
Sulfonamido			

idazole in which both the basicity (B_t) and acidity (A_w) are enhanced through the operation of resonance.



Imidazole Its Conjugate Acid Its Conjugate Base

THE ISOPROTIC POINT

It was seen earlier how the pK_a's of a polyprotic acid-base system could be employed to characterize the ampholytes in the system. Bicarbonate ion was found to be predominantly basic ($pK_{a_2} = 10.7$; $pK_{b_1} = 7.5$) although both functions are weak. Another method of employing the pK_a's of a diprotic acid for this purpose is to determine the pH at which the ampholyte is in equilibrium with *equivalent* concentrations of the diprotic acid and base; that is, for example, the pH at which $[H_2X] = [X^{--}]$. In the case of anionic and cationic ampholytes, this pH has been called the *first equivalence point* or *half neutralization point*. For uncharged or dipolar ionic ampholytes it has been termed the *isoelectric point*. A generic term to cover both of these is suggested; *i. e.*, the *isoprotic point*. The derivation of the equation connecting the isoprotic point, pH_I, with the pK_a's of a diprotic acid is given below.[3]

Process	*Constant*
$H_2X + H_2O \rightleftharpoons H_3O^+ + HX^-$	K_{a_1}
$HX^- + H_2O \rightleftharpoons H_3O^+ + X^{--}$	K_{a_2}
$H_2X + 2H_2O \rightleftharpoons 2H_3O^+ + X^{--}$	$K_{a_1}K_{a_2}$

$$\frac{[H_3O^+]^2[X^{--}]}{[H_2X]} = K_{a_1}K_{a_2}$$

At the isoprotic point:

$$[H_2X] = [X^{--}]$$

hence:

$$[H_3O^+]_I = \sqrt{K_{a_1}K_{a_2}}$$

or:

$$pH_I = {}^1/_2(pK_{a_1} + pK_{a_2})$$

The isoprotic point (half-neutralization point or isoelectric point) is equal to one-half the sum of the two pK_a's involved. For bicarbonate ion, for example, $pH_I = {}^1/_2\ (6.5 + 10.7) = 8.6$. The fact that this is greater than seven also indicates that the basicity of bicarbonate ion exceeds its acidity in strength.

THE DISMUTATION EQUILIBRIUM

The proportions of the three species, diprotic acid, ampholyte, and diprotic base, present at the isoprotic point are determined as follows.[3]

Process	*Constant*
$H_2X + H_2O \rightleftharpoons H_3O^+ + HX^-$	K_{a_1}
$H_3O^+ + X^{--} \rightleftharpoons HX^- + H_2O$	$1/K_{a_2}$
$H_2X + X^{--} \rightleftharpoons 2HX^-$	K_{a_1}/K_{a_2}

$$\frac{[HX^-]^2}{[H_2X][X^{--}]} = K_{a_1}/K_{a_2}$$

If:

$$[H_2X] = [X^{--}]$$

then:

$$\frac{[HX^-]}{[X^{--}]} = \frac{[HX^-]}{[H_2X]} = \sqrt{K_{a_1}/K_{a_2}}$$

When K_{a_1}/K_{a_2} has the minimum value of four, $[HX^-]/[H_2X]$ at pH_I equals two. Hence, $[H_2X] : [HX^-] : [X^{--}] = 1 : 2 : 1$, and 50 per cent of the total species is ampholyte. The greater the ratio of K_{a_1}/K_{a_2}, the more stable is the ampholyte species relative to its two conjugates. Thus, in the case of the bicarbonate ion, the species H_2CO_3, HCO_3^-, and CO_3^{--} occur in the ratio, 1 : 126 : 1 at the isoprotic point.

In the case of higher polyprotic acids, the pH_I of a given amphoteric species is equal to one-half the sum of *its* pK_a plus the pK_a corresponding to its pK_b (*i. e.*, the pK_a of the preceding species). Thus, the pH_I of $H_2PO_4^-$ is equal to ${}^1/_2\ (2.0 + 7.2) = 4.6$, while that of HPO_4^{--} is equal to ${}^1/_2\ (7.2 + 12.4) = 9.8$. Here again these figures reflect the character of the species, $H_2PO_4^-$ being predominantly acidic while HPO_4^{--} is predominantly basic.

The method given in the preceding paragraph may be particularly useful in calculating the isoelectric points of polyaminocarboxylic acids, aminopolycarboxylic acids, and polyaminopolycarboxylic acids, but before discussing these problems another question must be considered.

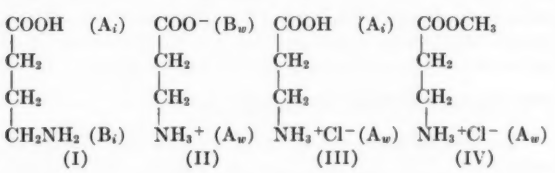
THE TAUTOMERIC EQUILIBRIUM

A substance such as γ-aminobutyric acid may be written in two different ways (I, II). The difference

TABLE 8
Species Inventory for the γ-Aminobutyric Acid System

Species[a]	*—Dominant constants—* pK_a's	pK_b's	*Character*
$^+NH_3CH_2CH_2CH_2COOH$	(1) 4.2	...	Diprotic acid
$^+NH_3CH_2CH_2CH_2COO^-$	(2) 10.4	(1) 9.8	Ampholyte
$[NH_2CH_2CH_2CH_2COOH]$			
$NH_2CH_2CH_2COO^-$	...	(2) 3.6	Diprotic base

[a] Minor species of the same net charge as the principal species are given in brackets. The principal and minor species are tautomers.



between these two structures involves a proton transfer from the carboxyl to the amino group so that equilibrium between these structures may be expected. To predict which of these structures predominates one must refer to the acidity of monocarboxylic acids and the basicity of aliphatic amines. The following systematic procedure is recommended:

(1) Add a proton to the ampholyte. Both structures (I) and (II) yield (III) which is the unambiguous, diprotic acid.

(2) Classify the acidic groups in (III) (use Table 7). In the present case the carboxyl group is A_i, the aliphatic ammonium ion, A_w.

(3) Regenerate the ampholyte by removing a proton from the diprotic acid, taking the proton predominantly from the stronger acidic group; in this case, therefore, from the carboxyl group. This yields (II) as the predominant structure of the amino acid (B_wA_w).

The conclusion reached concerning the dipolar ion structure of γ-aminobutyric acid may be arrived at more directly by comparing the pK_{a_1} of (III) (4.2) with the pK_a of the corresponding methyl ester hydrochloride (IV), (9.7). This discrepancy suggests that the pK_{a_1} of (III) does not correspond to the protolysis of the ammono group and hence it must correspond to the protolysis of the carboxyl group (actually to their sum) resulting in the formation of the dipolar ion as the predominant amphoteric species. A species inventory of this system is given in Table 8. Quantitatively,[9] the ratio of [II]/[I] is given by the ratio $K_{a_1} - K_{a\text{ester}}/K_{a\text{ester}}$ and amounts to $10^{5.5}$. The proportions of diprotic acid and diprotic base also present may be calculated as shown above in the case of bicarbonate ion (the dismutation equilibrium).

TABLE 9
Species Inventory for the *p*-Aminobenzoic Acid System

Species[a]	*—Dominant constants—* pK_a's	pK_b's	*Character*
$^+NH_3C_6H_4COOH$	(1) 2.3	...	Diprotic acid
$NH_2C_6H_4COOH$	(2) 4.9	(1) 11.7	Ampholyte
$[^+NH_3C_6H_4COO^-]$			
$NH_2C_6H_4COO^-$	...	(2) 9.1	Diprotic base

[a] Minor species of the same net charge as the principal species are given in brackets. The principal and minor species are tautomers.

The method of comparing the first constant of the amino acid hydrochloride with that of its ethyl ester hydrochloride is illuminating in the case of *p*-aminobenzoic acid for which the pertinent constants are, respectively, pK_{a_1} 2.3, and $pK_{a\text{ester}}$ 2.4. Here the formation of the ampholyte from the diprotic acid does involve the ammono group and the predominant amphoteric species is the uncharged molecule (Table 9).

A species inventory of the polyprotic acid-base system which includes β,γ-diaminobutyric acid yields the results given in Table 10. The ampholyte of zero net charge (to which the term *isoelectric point* applies) has the acidity of pK_{a_2} and the basicity of pK_{b_2}. Its isoelectric point, therefore, equals $^1/_2$ ($pK_{a_2} + pK_{a_3}$). Assuming the acidity constants to have the values 4, 10, and 11, $pH_I = 10.5$.

AMPHOTERIC SALTS

A common type of ampholyte which has not received general recognition as such is neither a molecule nor a single ion but a salt consisting of *two* ions. The cation (the conjugate of an uncharged base) is responsible for the acidic properties of the salt, and the anion (the conjugate of an uncharged acid) supplies the basic properties. Ammonium acetate is an example of such an ampholyte.

Unlike the ampholytes previously discussed, these salts are not related to diprotic acids and bases but to two different monoprotic acids and bases. The algebra involved in their treatment, however, is much the same provided that pK_{a_1} refers to the related uncharged acid, and pK_{b_2} to the related uncharged base. Thus:

Process	*Constant*
$HA + H_2O \rightleftharpoons H_3O^+ + A^-$	K_{a_1}
$BH^+ + H_2O \rightleftharpoons H_3O^+ + B$	K_{a_2}

Adding:

$$HA + BH^+ + 2H_2O \rightleftharpoons 2H_3O^+ + A^- + B \qquad K_{a_1}K_{a_2}$$

and:

$$K = \frac{[H_3O^+]^2\,[A^-]\,[B]}{[BH^+][HA]} = K_{a_1}K_a$$

At the isoprotic point:

$$[BH^+] = [A^-]$$

hence:

$$[HA] = [B]$$
$$[H_3O^+] = K_{a_1}K_{a_2}$$
$$pH_I = {}^1/_2(pK_{a_1} + pK_{a_2})$$

[9] EDSALL, J. T., AND M. H. BLANCHARD, *J. Am. Chem. Soc.*, **55**, 2337 (1933); COHEN, E. J., AND J. T. EDSALL, "Proteins, Amino Acids and Peptides as Ions and Dipolar Ions," Reinhold, New York, **1943**, p. 99.

TABLE 10
Species Inventory for the β,γ-Diaminobutyric Acid System

Species[a]	Dominant constants: Acidity	Dominant constants: Basicity	Character
$^+NH_3CH_2CH(NH_3^+)CH_2COOH$	pK_{a_1}	...	Cationic acid
$^+NH_3CH_2CH(NH_3^+)CH_2COO^-$	pK_{a_2}	pK_{b_1}	Cationic ampholyte
$[^+NH_3CH_2CH(NH_3)CH_2COOH]$		pK_{b_2}	Dipolar ampholyte (zero net charge)
$^+NH_3CH_2CH(NH_3)CH_2COO^-$	pK_{a3}		
$[NH_2CH_2CH(NH_3^+)CH_2COO^-$; NH_2CH_2-$CH(NH_2)CH_2COOH]$			
$NH_2CH_2CH(NH_2)CH_2COO^-$	...	pK_{b_2}	Anionic base

[a] Minor species of the same net charge as the principal species are given in brackets. The principal and minor species are tautomers.

The isoprotic point in this case is similar to the isoelectric point in that it is the pH at which the number of cations in the system is equal to the number of anions, and the net charge of the species in the acid-base reaction under consideration is zero.

Further information concerning the amphoteric salt may be obtained from the following derivation.

Process	Constant
$HA + H_2O \rightleftharpoons H_3O^+ + A^-$	K_{a_1}
$H_3O^+ + B \rightleftharpoons BH^+ + H_2O$	$1/K_{a_2}$

Adding:

$$HA + B \rightleftharpoons BH^+ + A^- \qquad K_{a_1}/K_{a_2}$$

$$K = \frac{[BH^+]\,[A^-]}{[HA]\,[B]} = \frac{K_{a_1}}{K_{a_2}} = \frac{K_w}{K_{a_2}K_b}$$

At the isoprotic point:

$$\frac{[BH^+]}{[B]} = \frac{[A^-]}{[HA]} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

The ratio K_{a_1}/K_{a_2} is a measure of the stability of the salt. If $K_{a_1} = K_{a_2}$ (that is, if $pK_{a_2} + pK_{b_1} = 14$), the salt will be half converted to its uncharged progenitors when dissolved in an aqueous solution having a pH = pH_I. If K_{a_1}/K_{a_2} is large (that is, if $pK_{a_2} + pK_{b_1} > 14$), the salt will be stable relative to its uncharged progenitors; while if K_{a_1}/K_{a_2} is small (that is, if $pK_{a_2} + pK_{b_1} < 14$), the salt will be largely transformed into its uncharged progenitors in aqueous solution.

In the case of ammonium acetate, for example, using the rounded values of 5 and 9 for the pK_a's of acetic acid and ammonium ion, respectively, one obtains a pH_I of 7 and a ratio of [AcOH] : [Salt] : [NH_3] at the isoprotic point of 1 : 100 : 1. Furthermore, ammonium acetate is to be classified as a weak base ($pK_{b_1}' = 9$) and a weak acid ($pK_{a_2} = 9$). The close relationship of such salts to other ampholytes may be seen in the species inventory given in Table 11.

INSOLUBLE AMPHOLYTES

The occurrence of amphoteric properties in slightly soluble substances is evidenced by their increased solubility in acidic and basic solutions. The simultaneous equilibria involved may be expressed as follows. Let HY represent a simple, slightly soluble ampholyte of zero net charge, such as phenylalanine, $PhCH_2CH(NH_3^+)COO^-$. In acidic solutions the following processes will occur.

Process	Constant
HY (solid) $\rightleftharpoons$ HY (dslvd.)	K_s
$H_3O^+ + HY$ (dslvd.) $\rightleftharpoons H_2Y^+ + H_2O$	$1/K_{a_1}$
$H_3O^+ + HY$ (solid) $\rightleftharpoons H_2Y^+ + H_2O$	K_s/K_{a_1}

$$\frac{[H_2Y^+]}{[H_3O^+]} = \frac{K_s}{K_{a_1}}$$

The observed solubility, $S = [HY]_{dslvd.} + [H_2Y^+]$. Hence:

$$S = K_s + \frac{K_s[H_3O^+]}{K_{a_1}} = K_s\left(1 + \frac{[H_3O^+]}{K_{a_1}}\right)$$

In solutions of bases, on the other hand, the following relationships occur:

Process	Constant
HY (solid) $\rightleftharpoons$ HY (dslvd.)	K_s
HY (dslvd.) + $OH^- \rightleftharpoons H_2O + Y^-$	$1/K_{b_2}$
HY (solid) + $OH^- \rightleftharpoons H_2O + Y^-$	K_s/K_{b_2}

$$\frac{[Y^-]}{[OH^-]} = \frac{K_s}{K_{b_2}}$$

therefore:

$$[Y^-] = \frac{K_s[OH^-]}{K_{b_2}} = \frac{K_sK_{a_2}}{[H_3O^+]}$$

The observed solubility, $S = [HY]_{dslvd.} + [Y^-]$. Hence:

$$S = K_s + \frac{K_sK_{a_2}}{[H_3O^+]} = K_s\left(1 + \frac{K_{a_2}}{[H_3O^+]}\right)$$

Thus, in the case of simple, slightly soluble ampholytes the solubility in acidic buffers will increase in proportion to the hydrogen-ion concentration (if $[H_3O^+]/K_{a_1}$ is large compared with unity), the proportionality factor being K_s/K_{a_1}. Likewise, the solubility in basic buffers will vary inversely as the hydrogen-ion concentration (if $K_{a_2}/[H_3O^+]$ is large compared to unity), the proportionality factor being $K_sK_{a_2}$.

TABLE 11
Species Inventory of the Ammonium Acetate System

Species	Dominant constants: Acidity	Dominant constants: Basicity	Character
AcOH; NH_4^+	pK_a of AcOH	...	Monoprotic acids
AcO^-; NH_4^+	pK_a of NH_4^+	pK_b of AcO^-	Amphoteric salt
AcO^-; NH_3	...	pK_b of NH_3	Monoprotic bases

TABLE 12
pH Ranges of Solutions of Acids and Bases

Concentration	*pH range for solutions of acids*	*pH range for solutions of bases*	*Concentration*
10^{-1} *M*	1.....7	7.....13	10^{-1} *M*
10^{-2}	2.....7	7.....12	10^{-2}
10^{-3}	3.....7	7.....11	10^{-3}
10^{-4}	4.....7	7.....10	10^{-4}
10^{-5}	5.....7	7.....9	10^{-5}
10^{-6}	6.....7	7.....8	10^{-6}
10^{-7}	6.79–7	7–7.21	10^{-7}
10^{-8}	7	7	10^{-8}

In the discussion given above the concentration of the diprotic base has been neglected in acidic solution, that of the diprotic acid in basic solution. In the pH region where both of these concentrations are significant, the observed solubility is given by:

$$S = [HY]_{\text{dslvd.}} + [H_2Y^+] + [Y^-]$$

The pH at minimum solubility may be derived as follows. Substituting:

$$S = K_s + \frac{K_s}{K_{a_1}}[H_3O^+] + \frac{K_sK_{a_2}}{[H_3O^+]}$$

Differentiating:

$$\frac{dS}{d[H_3O^+]} = \frac{K_s}{K_{a_1}} - \frac{K_sK_{a_2}}{[H_3O^+]^2}$$

Setting the differential equal to zero and solving:

$$[H_3O^+] = \sqrt{K_{a_1}K_{a_2}}$$

That is, the solubility of a slightly soluble ampholyte is a minimum in a buffer of pH equal to its isoelectric point.

THE pH's OF AMPHOLYTE SOLUTIONS

An ampholyte which has acidic and basic properties of equal strength ($pK_{a_2} = pK_{b_1}$; $pH_I = 7$) forms solutions in pure water which have a pH of 7. Other ampholytes yield acidic or basic solutions depending upon which function of the ampholyte is stronger. The pH's of their solutions fall between 7 and the pH_I, approaching the latter as the concentration increases.

Before examining the pH's of ampholyte solutions further it may be useful to consider the pH's of solutions of simple acids or bases. At the 0.1 *M* level, for example, *strong*, monoprotic acids have a pH of 1, *feeble* acids of $pK_a > 15$, a pH of 7. The intervening *intermediate* and *weak* acids form 0.1 *M* solutions having pH's between 1 and 7. As the concentration decreases, the pH range of solutions of acids becomes narrower; thus, at 10^{-3} *M* it extends from 3 to 7, at 10^{-5} *M* from 5 to 7, and so on (Table 12). The exact relationship between $[H_3O^+]$, *C*, the concentration of the acid-base system, and K_a is given by the third-order equation:[10]

$$[H_3O^+]^3 + K_a[H_3O^+]^2 - (CK_a + K_w)[H_3O^+] - K_aK_w = 0$$

Since this equation cannot be solved directly, methods of approximation are desirable. The relationships given in Table 13 are useful for solutions of acids whose concentrations are greater than 10^{-6} molar. Similar relationships apply for solutions of bases if pH is replaced by pOH and pK_a by pK_b; the pH is then obtained from the relationship, pH = 14 − pOH.

TABLE 13
Formulas for Calculating the pH's of Solutions of Acids

$pK_a + pC$	$pK_a - pC$	*pH*
<12	>3	$\frac{1}{2}(pK_a + pC)$
"	<3	$p\alpha + pC$
>12 but <16	>3	$7 - \log\sqrt{1 + \frac{K_aC}{K_w}}$
"	<3	$-\log\sqrt{(1-\alpha)CK_a + K_w}$
>16	...	7

The first of the expressions given in Table 13 is derived from the approximate form of Ostwald's dilution law, $\alpha^2C = K_a$. It neglects the ionization of water and considers [HA] = *C*. The second relationship is the logarithmic form of the expression $[H_3O^+] = \alpha C$, and also neglects the ionization of water. The third equation is derived from the expressions for K_a and K_w and the electrical balance, $[H_3O^+] = [OH^-] + [A^-]$. This does not neglect the ionization of water but considers [HA] = *C*. Substituting in the equation for electrical balance:

$$\begin{aligned}
[H_3O^+] &= \frac{K_w}{[H_3O^+]} + \frac{K_aC}{[H_3O^+]} \\
[H_3O^+]^2 &= K_w + K_aC \\
[H_3O^+] &= \sqrt{K_w + K_aC} \\
&= \sqrt{K_w + \frac{K_wK_aC}{K_w}} \\
&= \sqrt{K_w}\sqrt{1 + \frac{K_aC}{K_w}} \\
\text{pH} &= 7 - \log\sqrt{1 + \frac{K_aC}{K_w}}
\end{aligned}$$

The term $p\alpha$ which occurs in the second of the approximate formulas given above may readily be calculated in the following way. Ostwald's dilution law:

$$\frac{\alpha^2C}{1-\alpha} = K$$

may be transposed to:

$$\left(\frac{C}{K}\right)\alpha^2 + \alpha - 1 = 0$$

Solving for α:

$$\alpha = \frac{-1 \pm \sqrt{1 + 4\left(\frac{C}{K}\right)}}{2\left(\frac{C}{K}\right)}$$

Some values of α are given in Table 14.

The term $\log\sqrt{1 + K_aC/K_w}$, which also appears (and recurs later) is tabulated in Table 15.

The exact relationship between the hydrogen-ion

[10] PARK, B., J. CHEM. EDUC., **30**, 257 (1953).

TABLE 14
Values of pα

$pK - pC$	α	$p\alpha$	$pK - pC$	α	$p\alpha$	$pK - pC$	α	$p\alpha$
−3.0	0.999	0.0004	−0.6	0.828	0.082	1.8	0.118	0.928
−2.9	0.999	0.0005	−0.5	0.798	0.098	1.9	0.106	0.974
−2.8	0.999	0.0007	−0.4	0.766	0.116	2.0	0.0951	1.022
−2.7	0.998	0.0008	−0.3	0.732	0.135	2.1	0.0852	1.070
−2.6	0.998	0.0010	−0.2	0.695	0.161	2.2	0.0763	1.117
−2.5	0.997	0.0013	−0.1	0.657	0.182	2.3	0.0683	1.166
−2.4	0.996	0.0017	0.0	0.618	0.209	2.4	0.0611	1.214
−2.3	0.995	0.0023	0.1	0.579	0.237	2.5	0.0547	1.262
−2.2	0.994	0.0027	0.2	0.539	0.268	2.6	0.0489	1.311
−2.1	0.992	0.0034	0.3	0.500	0.301	2.7	0.0438	1.359
−2.0	0.990	0.0043	0.4	0.463	0.334	2.8	0.0390	1.409
−1.9	0.988	0.0052	0.5	0.426	0.371	2.9	0.0349	1.457
−1.8	0.985	0.0066	0.6	0.391	0.408	3.0	0.0311	1.509
−1.7	0.981	0.0083	0.7	0.358	0.446	3.1	0.0278	1.556
−1.6	0.976	0.010	0.8	0.327	0.485	3.2	0.0248	1.606
−1.5	0.970	0.013	0.9	0.297	0.527	3.3	0.0221	1.655
−1.4	0.963	0.016	1.0	0.270	0.569	3.4	0.0198	1.704
−1.3	0.954	0.020	1.1	0.245	0.611	3.5	0.0176	1.754
−1.2	0.944	0.025	1.2	0.222	0.654	3.6	0.0157	1.803
−1.1	0.931	0.031	1.3	0.200	0.699	3.7	0.0140	1.853
−1.0	0.916	0.038	1.4	0.181	0.742	3.8	0.0125	1.903
−0.9	0.898	0.047	1.5	0.163	0.788	3.9	0.0112	1.952
−0.8	0.878	0.057	1.6	0.146	0.826	4.0	0.0100	2.000
−0.7	0.854	0.068	1.7	0.132	0.879			

concentration and the concentration of a simple amphoteric salt of the type BH^+A^- is given by a fourth-order equation.[10] A thorough treatment of this problem has recently been published.[11] An approximate relationship may be derived as follows.

The species present in a solution of such an ampholyte are H_3O^+, OH^-, B, BH^+, HA, and A^-. Electrical balance requires that:

$$[H_3O^+] + [BH^+] = [OH^-] + [A^-]$$

while mass balance requires that:

$$[HA] + [A^-] = [B] + [BH^+]$$

Addition of these equations yields:

$$[H_3O^+] + [HA] = [OH^-] + [B]$$

For acidic ampholytes, $[OH^-]$ may be neglected. Substituting for [HA] and [B] the expressions obtained from the acidity constants of HA and BH^+ yields:

$$[H_3O^+] = \sqrt{\frac{K_{a_2}K_{a_2}[BH^+]}{K_{a_1} + [A^-]}}$$

If the ionic species are stable relative to their conjugates (that is, they are weak or intermediate bases in moderate concentrations), the concentration of the salt, C, may be substituted for $[BH^+]$ and $[A^-]$, and the expression becomes:

$$[H_3O^+] = \sqrt{\frac{K_{a_1}K_{a_2}C}{K_{a_1} + C}}$$

This formula was first derived by Noyes[12] and is commonly recommended for obtaining the pH's of acidic ampholytes.[13] Factoring gives:

$$[H_3O^+] = \sqrt{K_{a_2}C}\sqrt{\frac{K_{a_1}}{K_{a_1} + C}}$$

or:

$$[H_3O^+] = \sqrt{K_{a_2}C} \Big/ \sqrt{1 + \frac{K_b C}{K_w}}$$

that is:

$$pH = {}^1/_2(pK_{a_2} + pC) + \log \sqrt{1 + \frac{K_b C}{K_w}}$$

TABLE 15
Values of $\log \sqrt{1 + \frac{KC}{K_w}}$

$pK + pC$	$\log \sqrt{1 + \frac{KC}{K_w}}$	$pK + pC$	$\log \sqrt{1 + \frac{KC}{K_w}}$
12.0	1.002	14.1	0.127
12.1	0.953	14.2	0.106
12.2	0.903	14.3	0.088
12.3	0.854	14.4	0.074
12.4	0.805	14.5	0.060
12.5	0.757	14.6	0.048
12.6	0.709	14.7	0.039
12.7	0.661	14.8	0.032
12.8	0.613	14.9	0.026
12.9	0.567	15.0	0.021
13.0	0.521	15.1	0.017
13.1	0.474	15.2	0.013
13.2	0.432	15.3	0.011
13.3	0.390	15.4	0.009
13.4	0.349	15.5	0.007
13.5	0.310	15.6	0.005
13.6	0.273	15.7	0.004
13.7	0.238	15.8	0.003
13.8	0.206	15.9	0.003
13.9	0.177	16.0	0.002
14.0	0.150		

[11] Ricci, J. E., "Hydrogen Ion Concentration," Princeton University Press, Princeton, N. J., 1952.
[12] Noyes, A. A., *Z. physik. Chem.*, 11, 495 (1893).
[13] Glasstone, S., "Textbook of Physical Chemistry," 2nd ed., D. Van Nostrand Co., Inc., New York, 1946.

The first factor is seen to yield the pH which would prevail if the acid group alone were present (provided $pK_a + pC < 12$ and $pK_a - pC > 3$). The second factor is, therefore, the correction due to the effect of the basic group. (See Table 15.)

The usefulness of this formula may be enhanced by replacing the first factor when necessary by one of the alternative approximations given above for the pH of a solution of an acid, and then applying the correction (second factor). For basic ampholytes a similar formula:

$$pOH = \sqrt{\frac{K_{b_1}K_{b_2}C}{K_{b_1} + C}}$$

may be employed, the pH being calculated from the relationship pH = 14 − pOH.

The rules for calculating the pH's of solutions of simple ampholytes may be summarized as follows. (Note: In the following calculations pK_{a_2} and pK_{b_1} are to be employed if their sum ≧ 14.6 (14.0 for amphoteric salts). Otherwise, the ampholyte is largely transformed into its conjugate species and pK_{a_1} and pK_{b_2} are to be employed instead.)

(1) If $pK_{a_2} + pC$ and $pK_{b_1} + pC$ both < 12, the isoelectric point, $pH_I = {}^1/_2(pK_{a_1} + pK_{a_2})$, is a good approximation of the pH.

(2) If $pK_{a_2} + pC < 12$ and $pK_{b_1} + pC > 12$, calculate the pH from the acid constant alone and *add* the correction:

$$\log \sqrt{1 + \frac{K_{b_1}C}{K_w}}$$

If $pK_{b_1} + pC > 16$, the correction is negligible.

(3) If $pK_{a_2} + pC > 12$ and $pK_{b_1} + pC < 12$, calculate the pOH from the basic constant alone, transform this to pH (pH = 14 − pOH) and *subtract* the correction:

$$\log \sqrt{1 + \frac{K_{a_2}C}{K_w}}$$

If $pK_{a_2} + pC > 16$, the correction is negligible.

(4) If both $pK_{a_2} + pC$ and $pK_{b_1} + pC > 12$, assume a pH of 7 and apply both the corrections given in (2) and (3).

The calculations discussed above may be illustrated by means of the three ampholytes given in Table 16. While all three have an isoelectric point of 5, the pH's of their aqueous solutions differ, the difference being the greater the more dilute the solution.

TABLE 16
Calculated pH's of Some Ampholyte Solutions

Concentration	pK_{a_1}	pK_{a_2}	pK_{b_1}	*pH, calculated*	pH_I
10^{-1} *M*	4.00	6.00	10.00	5.00	5.00
10^{-1} *M*	3.00	7.00	11.00	5.00	5.00
10^{-1} *M*	2.00	8.00	12.00	5.02	5.00
10^{-3} *M*	4.00	6.00	10.00	5.02	5.00
10^{-3} *M*	3.00	7.00	11.00	5.15	5.00
10^{-3} *M*	2.00	8.00	12.00	5.52	5.00
10^{-5} *M*	4.00	6.00	10.00	5.59	5.00
10^{-5} *M*	3.00	7.00	11.00	6.02	5.00
10^{-5} *M*	2.00	8.00	12.00	6.48	5.00

THREE-CONSTANT AMPHOLYTES

Amphoteric salts of the type BH^+HX^- are derived from monoprotic bases, B, and diprotic acids, H_2X; they involve three acidity constants: K_{a_1} and K_{a_2} for H_2X, and K_{a_3} for BH^+. The problem of the pH's of aqueous solutions of such salts has recently been considered in the literature.[11,14] While formulas involving three acidity constants have been employed in these cases, many salts of this type respond to simpler treatment if a preliminary scanning indicates that one or even two of the three constants may not be significant. The following examples have been chosen because direct comparison with Ricci's treatment[15] may be made in these cases.

Example 1. Ammonium bicarbonate, $NH_4^+HCO_3^-$; pK_{a_2} 9; pK_{b_1} 7; pK_{a_1} 11.

Since $pK_{a_2} + pK_{b_1} = 16$, and $pK_{a_2} + pK_{b_2} = 18$, the ions shown are stable species. In the presence of ammonium ion (pK_{a_2} 9), the acidity of bicarbonate ion (pK_{a_1} 11) is negligible. Hence, the isoprotic point of ammonium bicarbonate = ${}^1/_2(pK_{a_1} + pK_{a_2}) = 8$, and solutions 10^{-3} *M* or stronger have approximately this pH.

Example 2. Ammonium bisulfite, $NH_4^+HSO_3^-$; pK_{a_2} 9; pK_{b_1} 12; pK_{a_1} 7.

Here the acidity of the ammonium ion (pK_{a_2} 9) is negligible in the presence of bisulfite ion (pK_{a_1} 7). Furthermore, $pK_{b_1} + pK_{a_2} = 19$; hence the species shown are stable. The isoprotic point = ${}^1/_2$ ($pK_{a_1} + pK_{a_2}$) = 4.5, and the pH's of solutions of this salt are not materially different from those of sodium bisulfite.

Example 3. Sodium ammonium carbonate, $Na^+NH_4^+CO_3^{--}$ (pK_{a_2} 9; pK_{b_2} 3) ⇌ $Na^+HCO_3^-$ + NH_3 (pK_{b_1} 7; pK_{a_2} 11; pK_{b_2} 5.)

Since $pK_{a_2} + pK_{b_2} = 12$ (that is, less than 14), the ionic species of the original salt are not stable in solution, the salt being largely transformed to a mixture of sodium bicarbonate and ammonia ($pK_{a_2} + pK_{b_1} = 16$). The basicity of ammonia (pK_b 5) outweighs that of bicarbonate ion (pK_{b_1} 7); hence, the isoprotic point = ${}^1/_2$ ($pK_{a_2} + pK_{a_1}$) = 10.

Example 4. Ammonium carbonate, $(NH_4^+)_2CO_3^{--}$ (pK_{a_2} 9; pK_{b_2} 3) ⇌ $NH_4^+HCO_3^-$ + NH_3 (pK_{a_2} 9; pK_{b_1} 7; pK_{a_1} 11; pK_{b_2} 5).

Here, too, the salt given is unstable in solution, being largely transformed to ammonium bicarbonate and ammonia. The acidity and basicity of bicarbonate ion are negligible by comparison with the acidity of ammonium ion and the basicity of ammonia, respectively. Here, therefore, the pH_I is the pH of the 1 : 1 NH_4^+:NH_3 buffer; *i. e.*, the pK_a of ammonium ion, or 9.

The exact equation connecting the hydrogen-ion concentration of solutions of salts of the type BH^+-

[14] Eeckhout, J., *Anal. Chim. Acta*, **7**, 203 (1952); **9**, 197 (1953).

[15] Ricci, J. E., *loc. cit.*, p. 264.

HX^- (B is a monoprotic, uncharged base; H_2X a diprotic, uncharged acid) with their acidity constants is of the fifth order. Ricci[11] gives several approximations which may be employed but these are still fairly complicated. Eeckhout[14] has proposed a simpler approximation which, in harmony with the method given above for salts of the BH^+A^- type, may be derived as follows:

$[H_3O^+] + [BH^+] = [OH^-] + [HX^-] + 2[X^{--}]$ (electrical balance)
$[H_2X] + [X^{--}] + [HX^-] = [BH^+] + [B]$ (mass balance)

$[H_3O^+] + [H_2X] = [OH^-] + [X^{--}] + [B]$ (sum)

Substituting for $[H_2X]$, $[OH^-]$, $[X^{--}]$, and $[B]$, the expressions obtained from the acidity constants containing these respective terms yield:

$$[H_3O^+] + \frac{[H_3O^+][HX^-]}{K_{a_1}} = \frac{K_w}{[H_3O^+]} + \frac{K_{a_2}[HX^-]}{[H_3O^+]} + \frac{K_a[BH^+]}{[H_3O^+]}$$

or:

$$[H_3O^+] = \sqrt{\frac{K_{a_1}(K_w + K_{a_2}[HX^-] + K_a[BH^+])}{K_{a_1} + [HX^-]}}$$

For acidic ampholytes $[OH^-]$ may be neglected. If, furthermore, the ampholyte is sufficiently stable so that its concentration, C, may be substituted for the ionic concentrations, the expression becomes:

$$[H_3O^+] = \sqrt{\frac{K_{a_1}(K_{a_2}C + K_a C)}{K_{a_1} + C}}$$

Factoring:

$$[H_3O^+] = \sqrt{K_{a_2}C + K_a C}\sqrt{\frac{K_{a_1}}{K_{a_1} + C}}$$

$$= \frac{\sqrt{K_{a_2}C + K_a C}}{\sqrt{1 + \frac{K_{b_1}C}{K_w}}}$$

Comparison of this formula with that given above for simple ampholytes shows that the "correction factor" for the basic group is the same; but the hydrogen-ion concentration to which it is applied is here equal to the square root of the sum of the squares of the hydrogen-ion concentrations which would be shown by each acidic group if present alone (provided $pK_a + pC < 12$ and $pK_a - pC > 3$). The more accurate expression for each of these hydrogen-ion concentrations may be employed in place of $\sqrt{K_aC}$ when the criteria $pK_a + pC$ and $pK_a - pC$ demand it.

For basic ampholytes of the type BH^+HX^-, the relationship:

$$[OH^-] = \frac{\sqrt{K_{b_2}C}}{\sqrt{1 + \frac{K_{a_2}C}{K_w} + \frac{K_{a_2}C}{K_w}}}$$

applies. Here, too, the criteria $pK_{b_1} + pC$ and $pK_{b_1} - pC$ determine whether $\sqrt{K_{b_1}C}$ should be replaced by more accurate expressions.

Similar derivations lead to the following formulas. For acidic ampholytes of the type ZH^+A^- (Z represents an uncharged, diprotic base and HA an uncharged, monoprotic acid), the relationship:

$$[H_3O^+] = \frac{\sqrt{K_{a_1}C}}{\sqrt{1 + \frac{K_{b_1}C}{K_w} + \frac{K_{b_2}C}{K_w}}}$$

applies, in which K_{b_1} refers to A^- and K_{b_2} and K_{a_2} to ZH^+. Basic ampholytes of this type require the formula:

$$[OH^-] = \frac{\sqrt{K_{b_1}C + K_{b_2}C}}{\sqrt{1 + \frac{K_{a_2}C}{K_w}}}$$

The validity of the methods of calculating the pH's of ampholyte solutions discussed in the foregoing pages may be judged by the following tests. Ricci[11] gives 91 calculations of the pH's of ampholyte solutions. In 65 cases (71 per cent) the methods presented here gave identical results to the second decimal place; in 17 cases (19 per cent) the deviation was ± 0.01; in eight cases (nine per cent) the deviation was ± 0.02; and in only one case the deviation was $+0.03$. In one case in which a greater discrepancy was observed Ricci accidentally gives a C_H which yields a pH of 2.09 instead of 2.009.

Eeckhout's[14] calculations of the pH's of ampholyte solutions were also compared with the methods discussed above. Of 28 calculations, 16 cases (57 per cent) agreed to the second decimal place, five cases (18 per cent) deviated by ± 0.01, three cases (11 per cent) deviated by ± 0.02, and one case by -0.04. This last case (the pH of 0.1 M Na_2HPO_4; pK_{a_2} 12.3; pK_{b_2} 6.8) was given as having a pH of 9.75. The value of 9.71 obtained in the present calculation was checked by the method of Ricci and found to be correct.

Park[10] gives 18 calculations for the pH's of amphoteric salts. Of these, 13 cases (72 per cent) agreed to the second decimal place and five cases (28 per cent) agreed to within $+0.01$.

"The best equipment in any laboratory is still in the head of the man or woman running it."

OTTO M. SMITH, *1956 Recipient of the Scientific Apparatus Makers Award in Chemical Education*

A CHEMISTRY COURSE INCLUDING BOTH QUALITATIVE AND QUANTITATIVE ANALYSIS[1]

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SEVERAL years ago, as part of a general revision of the curriculum in chemistry at Washington and Jefferson College, the systematic presentation of qualitative inorganic analysis was removed from the second semester of general chemistry and was placed instead in the second-year chemistry course with quantitative analysis. It was felt that this was a natural step in the evolution of the chemistry curriculum. The modern course in general chemistry, with its expanded content and its increased emphasis on generalizations and theory, seemed to demand a different sort of laboratory experience from that provided by conventional qualitative analysis. Furthermore, the placing of qualitative analysis with quantitative analysis in the second year seemed justified because it brought together two subjects that have a common theoretical basis and a related purpose, even though their techniques and methods are often notably different.

As a consequence of this change in curriculum, the author was presented with the question: "How can qualitative and quantitative analysis be given in the same year most efficiently and most effectively?" Most institutions that face this question offer separate one-semester courses in qualitative and quantitative analysis, in that order. This is an abbreviated version of the traditional approach, which goes back more than 100 years. (Fresenius' textbooks on qualitative and quantitative analysis appeared in their first editions in 1841 and 1846, respectively.) The approach was certainly a sound one in the eighteen-forties when analytical chemistry was a much more empirical science, and when the main purpose of the courses was the production of trained analysts. Today, however, the situation is different. Chemistry has expanded along with the other sciences; organic chemistry and physical chemistry are in the curriculum, so that the place of analytical chemistry is less prominent; the phenomena of qualitative and quantitative analysis have been given a common interpretation through modern theories of atomic structure and chemical equilibria; instrumental methods, often supplying qualitative and quantitative information simultaneously, have supplanted in actual practice many of the traditional chemical procedures and have given the two fields of analysis more in common.

Reflection upon this changed situation caused the author and his colleagues to turn the original question into one that seemed to be more relevant as well as more fundamental: "What kind of one-year course, including at least portions of traditional qualitative and quantitative analysis, would serve as the best introduction to analytical chemistry for the second-year chemistry students of today?"

An imaginative answer to this question has been advanced by E. H. Swift,[2] who received the Fisher award in analytical chemistry this year, partly for his pioneering work in the teaching of analytical chemistry. Swift proposed that the traditional sequence of courses be reversed so that the introductory course in quantitative analysis might precede the course in qualitative analysis, which could then be made into a rigorous and quantitative course in chemical separations. Dunkelberger[3] has described a similar inverted course. Both authors feel that such a sequence facilitates the correlation of classroom instruction with laboratory work, equilibrium theory being thoroughly presented during the course in quantitative analysis and used in the second course to systematize the chemical properties of the various elements studied. West[4] also has expressed agreement on the need to correlate the course in qualitative analysis with the methods of quantitative analysis. He has noted in addition the growing trend toward including instrumental methods in the undergraduate curriculum.

This paper describes a one-year course in analytical chemistry which the author and his colleagues have developed in the past several years as a tentative answer to the question for Washington and Jefferson College.

DESCRIPTION AND OUTLINE OF THE COURSE

The course is entitled: The Theory and Practice of Analytical Chemistry, and is designed to be an introduction to the use of theory, fact, and technique in chemical analysis, principally inorganic chemical analysis. As given currently at Washington and Jefferson College, the course consists of two lecture-recitation periods and two three-hour laboratory periods per week, for two fifteen-week semesters. Premeds, who bulk rather large in the course, have the option of

[1] Presented before the Division of Chemical Education at the 127th Meeting of the American Chemical Society, Cincinnati, March, 1955.

[2] SWIFT, E. H., "A System of Chemical Analysis (Qualitative and Semi-Quantitative) for the Common Elements," Prentice-Hall, New York, 1939; J. CHEM. EDUC., 27, 677–9 (1950).

[3] DUNKELBERGER, T. H., *ibid.*, 27, 680–2 (1950).

[4] WEST, P. W., *ibid.*, 29, 222–3 (1952).

taking three instead of six laboratory hours per week during the second semester. Chemistry majors are required to take six hours of laboratory work per week throughout the year.

Particular attention has been given to organizing the laboratory work so that there will be a logical development of the topics of analytical chemistry. The division of the laboratory work is as follows:

Part I. Qualitative and Proximate Quantitative Analysis (10 weeks)
Part II. Semiquantitative Analysis (8 weeks)
Part III. Quantitative Analysis (7 weeks)
Part IV. Special Methods of Analysis ($2^1/_2$ weeks)
Part V. Studies of Methods for Chemical Separation ($2^1/_2$ weeks)

Proximate quantitative analysis is defined by the author as analysis where an accuracy of from one to three parts per ten is desired, *i. e.*, a rough estimation of amount or concentration. Semiquantitative analysis is defined as analysis where an accuracy of one part per hundred, or ten parts per thousand, is desired. Quantitative analysis has the usual meaning, an accuracy of one or two parts per thousand being desired.

Qualitative analysis is presented first, as a logical extension of the work of general chemistry, so that the students will have an opportunity to learn the relevant chemical properties of the various elements to a degree that is not possible in the first-year course. Theory is applied rather rigorously to the discussion of the chemical properties and the qualitative scheme, since the students have had a thorough introduction to atomic structure and chemical equilibria in their first year. In other words, the course in general chemistry has emphasized theory more than facts, so the course in analytical chemistry is begun with a strong emphasis on the facts, but from a theoretical point of view. For example, the oxidation states of tin, lead, arsenic, and antimony are interpreted using the concept of the "inert pair" of electrons; in writing equations an attempt is made to distinguish between the use of species such as H_3AsO_3 and $H_2AsO_3^-$, based on the approximate pH of the solution and the ionization constant of the weak acid; the chemical properties of the elements and the directions of reactions are deduced where possible from tables of equilibrium constants, after the manner of Hogness and Johnson.[5]

An attempt is made to bridge the customary and perhaps artificial gap between *crude* qualitative analysis and *exact* quantitative analysis by the introduction of some experiments on rough estimation of concentration along with the qualitative analysis in Part I, and by the introduction of semiquantitative analysis in Part II, where typical gravimetric and volumetric analyses are done at a lower level of accuracy and precision than is usual.

Part II, which extends into the second semester, is admittedly a departure from tradition. It attempts, in a shorter time than usual, to introduce the student to the various types of chemical method used in quantitative analysis. Many of the common operations of quantitative analysis are included in this part of the course, but because of the lower degree of accuracy and precision required, many common operations can be omitted. Samples often are not dried; standard solutions are prepared without taking special precautions, often by direct weighing; indicator blanks are the exception rather than the rule; burets are not calibrated; objects are weighed to the nearest milligram rather than to the nearest tenth of a milligram.

In Part III certain refinements of method and technique, such as those operations omitted in Part II, are introduced in order that a higher degree of accuracy may be achieved. Selected gravimetric and volumetric analyses are carried out at this higher level of accuracy and precision.

By carrying out many traditional quantitative determinations at a semiquantitative level of accuracy and precision, enough time is saved to permit the introduction of some special methods of analysis in Part IV, and one or more experiments of a semi-research nature in Part V. This last division of the laboratory work, where semiquantitative or quantitative methods are used to evaluate separation procedures such as the ones used in qualitative analysis, is intended to tie together both fields of analysis and serve as a stimulating climax to the entire course.

Experiments with instruments are staggered, because of limitations of equipment, so that Parts III and IV overlap to some extent in the actual scheduling of laboratory work.

The lectures parallel the laboratory work as closely as possible, and are grouped as follows: brief review of fundamental concepts (2 weeks); theory and practice of qualitative analysis (7 weeks); theory and practice of quantitative analysis (15 weeks); special methods and research in analytical chemistry (6 weeks).

EXPERIMENTS

The following is a typical list of the experiments done by chemistry majors.

Part I. Qualitative and Proximate Quantitative Analysis
- Checking and preparation of equipment
- Cation Group 0—preliminary experiments and unknown
- Determination of sensitivity of a Group 0 confirmatory test
- Proximate analysis for Group 0 cation, using limit of detection
- Cation Group I—unknown for qualitative analysis and for proximate quantitative analysis using volume of precipitate
- Cation Group II—preliminary experiments, known, and unknown
- Proximate colorimetric analysis, using visual method
- Cation Group III—known
- Cation Groups IV and V—known and unknown
- General cation unknown
- Development of original procedure for qualitative analysis of a group of five cations selected at random
- Special unknown, analyzed by the student's original procedure
- Anions—preliminary experiments, simple unknown, and mixed unknown

[5] Hogness, T. R., and W. C. Johnson, "Qualitative Analysis and Chemical Equilibrium," 4th ed., Henry Holt and Company, New York, 1954, p. 376.

Salts—identification of two simple salts
Special project (if time permits)

Part II. Semiquantitative Analysis
Preparation and cleaning of equipment
Exercise with analytical balance: weighing to the third place
Exercise with burets
Gravimetric: per cent H_2O in $CuSO_4 \cdot 5H_2O$
Volumetric:
Preparation and comparison of NaOH, HCl, and $H_2C_2O_4$ solutions
Standardization of NaOH with potassium acid phthalate
Analysis of impure potassium acid phthalate
Analysis of soda ash by direct titration with methyl orange
Direct preparation of standard $AgNO_3$ solution
Analysis of soluble chloride sample using chromate indicator
Analysis of a material of commerce: "Sani-Flush," for $NaHSO_4$ and NaCl on same sample

(End of first semester)

Direct preparation of standard $KMnO_4$ solution
Analysis of three per cent hydrogen peroxide solution
Check of $KMnO_4$ normality, using standard $H_2C_2O_4$ solution
*Standardization of $KMnO_4$ with pure sodium oxalate
Analysis of impure sodium oxalate
*Analysis of soluble iron sample using $SnCl_2$ method with $KMnO_4$
*Analysis of pyrolusite for "available oxygen," using standard $H_2C_2O_4$ solution and back titration with $KMnO_4$
Direct preparation of standard $K_2Cr_2O_7$ solution
Analysis of impure ferrous salt
*Demonstration of use of Jones reductor and ceric sulfate in analysis of a uranium salt

Part III. Quantitative Analysis
Calibration of a buret
Exercise with analytical balance: determining the sensitivity at various loads; weighing to the fourth place
Gravimetric: analysis of soluble chloride sample
Volumetric:
*Standardization of $KMnO_4$ with pure As_2O_3, repeated twice at one-month intervals to check on stability of solution
*Analysis of soluble arsenic sample using $KMnO_4$
*Check of $K_2Cr_2O_7$ normality using iron wire of known purity
*Analysis of iron ore using $K_2Cr_2O_7$
Preparation of $Na_2S_2O_3$ solution; standardization with pure Cu
*Check of $Na_2S_2O_3$ normality using standard $K_2Cr_2O_7$
Iodometric analysis of a copper solution
*Analysis of impure calcium carbonate; comparison of methods:
Gravimetric, as $CaC_2O_4 \cdot H_2O$, after drying at 90°C.
Gravimetric, as CaC_2O_4, after drying at 250–300°C.
Volumetric, titrating oxalate with $KMnO_4$

Part IV. Special Methods of Analysis
*Electrodeposition of Cu
*Analysis of nickel solution using dimethylglyoxime
Use of pH meter: calculation of K_i values from pH measurements
Use of electrophotometer: preparation of calibration curve for permanganate solutions; analysis of pyrolusite for manganese

Part V. Studies of Methods for Chemical Separation
Separation of iron from magnesium by NH_4OH precipitation: a class project, employing statistical design for selecting various ratios of $Fe:Mg:NH_3:NH_4^+$; precipitate filtered, washed, ignited, and weighed; filtrates checked with pH meter; actual separation compared with theoretical from K_i and K_{sp} values
*Special project according to student's interest

(Asterisk denotes experiments omitted by students taking only three laboratory hours per week during second semester.)

EVALUATION

This plan of laboratory experiments was instituted in the year 1953–54 and thus experience with its actual operation is limited. The author and his colleagues were pleased with the way students made the transition from Part I to Part II. With regard to the accuracy of the semiquantitative work, results obtained to date indicate that the average error of the individual student averages is around *eleven* parts per thousand for determinations done in this manner, as compared with an average error of around *seven* parts per thousand for the same determinations done in previous years in the quantitative manner. Results obtained from Part III of the course indicate that the quantitative experiments are being done as accurately as in previous years, but an average error of seven parts per thousand for such experiments does seem to leave considerable room for improvement.

It will be noted that some traditional determinations (*e. g.*, sulfate, limestone, brass) have not been included in the above list of experiments. Some of these could be included, at the instructor's option, in place of others that have been listed. At Washington and Jefferson College a one-semester course in advanced analytical chemistry is available to juniors and seniors, and it can include the classical determinations omitted in the introductory course, as well as other, more modern methods. The author holds no brief for the particular experiments chosen, but does feel that the idea of organizing the laboratory work along the lines indicated has real merit. It is felt that through such a course students will come to have a good grasp of the whole field of inorganic chemical analysis, along with good judgment as to the methods and techniques necessary to achieve a specified degree of accuracy and precision in a particular situation.

ACKNOWLEDGMENT

The revision of the curriculum in chemistry at Washington and Jefferson College was initiated by C. R. Waldeland, chairman of the chemistry department. The author is grateful to him, to other colleagues at Washington and Jefferson College, and to former colleagues at Emory University for inspiration and helpful discussions leading to the development of this course.

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WHAT A CHEMISTRY TEACHER SHOULD KNOW ABOUT OIL[1]

HOWARD C. ANDERSON
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WHAT kind of an industry is the oil business? It has been maligned by congressmen, praised by our generals and admirals, misunderstood by the public, and it is a favorite whipping-boy for the bureaucrats. But exactly what is the petroleum industry?

It is an industry of 42,075 businesses, covering refining, pipelines, production, marketing, packaging, leasing, storage, tank-car companies, trucking outfits, water and ocean shipping companies, fuel oil and LPG companies. More than 34 billion dollars is invested in these companies. Each company must work closely with the next in line, to keep the oil flowing smoothly from the oil sands below the earth to the customers' fuel tanks.

A hitch in any one phase could seriously impede our accustomed mode of life. We are a modern industry by many standards, and spend several billions of dollars each year to keep modern.

In general, the nonhydrocarbon content of petroleum ranges from 0.1 per cent to more than 15 per cent with water and sulfur as the basic contaminants. Petroleum ranges in color from a light amber, or almost colorless, through a dark green, to brown-green and black. It may be very fluid, or tar-like in consistency. Each crude presents its own peculiar problems in producing and refining.

Drillers have gone far into the earth. Can you imagine drilling a hole over four miles in depth? Ohio Oil Company did that last year at Paloma, California, when they drilled 21,482 feet before abandoning the venture as a duster. That is the present record depth, but by this time next year it may be broken. Unfortunately, the depth of producing wells has not kept up with the deepest holes drilled. The present record production depth is 17,892 feet.

THE CHEMIST'S ROLE

A chemist has very little active part in drilling operations. But in the development of the special drilling muds and fluids he has played an important part. These muds serve two primary purposes: first, to cool the drilling bit and remove the cuttings; and second, to present a formidable back pressure on the bottom of the hole to prevent the eruption of a gusher when gas or oil sands are opened. The mud is pumped down the center of the drill stem pipe, out around the bit, and up the outside of the pipe. This washes away the chips of rock which are cut loose by the rotating bit.

The term "oil reserves" refers to the oil we have discovered but which is still in the ground. We have now nearly 28 billion barrels, according to the 1952 year-end figures. We will have oil in abundance in this country if and when newer and better fuels become commercially available: atomic or solar energy, for example.

The largest role played by the chemist occurs in the refining aspect of the industry. What happens in a refinery? First we take a raw material, crude oil, and convert it to its many useful end products by a series of processes. The first process usually encountered is desalting. The chemist and physicist came to our aid many years ago by showing us how to get rid of these inorganic contaminants. Salts under high temperature and pressure can hydrolyze, forming HCl gas, and release in turn some H_2S from the sulfur-containing molecules. This has caused severe corrosion in the usual carbon-steel materials found in refinery pipes, tubes, and vessels. We desalt by adding water to the crude oil, emulsifying it, and breaking the emulsion with special chemicals and high-voltage electricity. From 95 to 98 per cent of the salt content of crude may be removed in this manner.

Next, the crude is heated and fed into a distillation tower. Here the various fractions of the crude are separated. The lighter the product the higher it boils in the tower and is drawn off at the appropriate tray or deck. Each tray has several holes with a riser on the top side. Over each riser is a bubble cap which resembles a giant toadstool. The edges of the caps are usually serrated. The action here is as follows: The boiling vapors from the lower deck pass up through the risers and down under the edge of the bubble caps through the boiling-liquid layer on this deck. Any portion of the vapors that would condense at this point go into the liquid phase. The balance passes on up the tower from tray to tray until it finds its condensing level.

On the other hand, the liquid phase may build up on the tray and spill over a dam on the side of the tray, passing down a chute called the downcomer. This takes the liquid down a tray to a hotter level. The portion that will boil here is freed, and the liquid portion continues dropping from tray to tray until it reaches its boiling level.

At appropriate sections in the tower, drawoffs

[1] From a paper presented before the Conference of High-school Chemistry Teachers, Laramie, Wyoming, August 9, 1954.

are made to remove as much product as is introduced into the tower. In a crude tower the drawoffs from top to bottom would be gas and gasoline at the top, light naphtha, heavy naphtha, distillates, diesel fuels, gas oils, and at the bottom a reduced crude fraction.

In general the operation of any fractionation tower is on the same principle as the crude tower just explained, whether we are fractionating lubricating oil or separating isobutane from *n*-butane.

CRACKING AND POLYMERIZATION

For years the operation just described was all that was done with crude, except to coke the reduced crude to get a maximum gas-oil yield. Then, on an old still, Dr. Burton put a valve on the end of the drawoff and permitted the heating to be done against the vapor back pressure. Thermal cracking resulted when long-chained or multi-branched hydrocarbons were fractured under the application of heat and pressure. An olefinic-type product results from this type of cracking.

Today thermal cracking has two distinct phases: vis-breaking, in which the larger waxy molecules are split (reducing the viscosity of the reduced crude); and vapor-phase cracking, in which the resultant gas oil from the vis-breaking operation is heated to beyond its critical temperature under pressure, to crack it into useful fractions like gasoline and butane.

For years this was as far as the refiner could go in the improvement of his product. Then an action the reverse of cracking was perfected; we call it polymerization. In cracking, a large portion of the gas-oil molecule is split into gases of the methane-to-butane range. A considerable portion of these are olefinic. The catalytic polymerization process uses a copper pyrophosphate-type catalyst to combine two or more of these olefinic gas molecules, which leaves us with an olefin multi-branched molecule of the gasoline range.

Certain selective processes to combine an olefin and a nonolefin were developed just prior to the war. This process is called alkylation. The catalyst employed here is either anhydrous hydrogen fluoride or fuming sulfuric acid. Incidentally, the famous isooctane (2,2,4-trimethyl pentane) is made by this process. It has that magic octane number of 100, which for years has been the goal of gasoline perfection. Today, compounds and certain blended aviation gasolines have much higher octane numbers than this.

Before the war many companies were doing research work on a new type of cracking. There was some limited cracking done in fixed-catalyst beds on special-feed stocks. Several pilot plants were also in operation on various types of moving-bed catalysts. The leaders of petroleum industry and officials of the Army and Navy met to decide whether to go into full-scale catalytic operations or build a trial plant or two. The decision was made to go into full production, and the defense "cat crackers" were ordered. The results were more than satisfactory.

Basically, a "cat cracker" cracks the gas-oil feed stock by the action of temperature alone on the oil in the presence of the catalyst. Cracking operations are done under only a few ounces of pressure. The catalyst in use varies from one process to another, but is usually an acid-treated bentonite or aluminum silicate.

The key to this catalyst activity is the large surface area in which the cracking can take place. A handful of catalyst has been estimated to contain several acres of surface. Other beneficial results accompanying catalytic cracking are desulfurization, hydrogenization, cyclization, and isomerization.

Other specific processes found in refineries are:

(1) *Stabilization*, which adjusts the butane content of gasoline: low in summer to prevent vapor locking of the motor, and high enough in the winter to promote easy engine starting.

(2) *Isomerization*, a process accomplished in the presence of anhydrous aluminum chloride which changes *n*-butane to isobutane for a sizable gain in octane number.

(3) *Reforming*, a modified cracking process by which heavy gasolines or naphthas are converted to high-octane gasolines. This may be either a thermal or a catalytic process.

(4) *Sweetening* (or desulfurization), the processes by which either the remaining sulfur compounds are removed or the objectionable-smelling sulfur compounds are converted to sweet-smelling ones.

In general these sweetening processes are quite important to the chemist. They all employ a regenerating step to reclaim and re-use the chemicals; this is the portion of refining where the chemist can claim his value many times over.

Some sweetening is done by using sodium plumbate (litharge and caustic soda) to remove H_2S and convert alkyl mercaptans to alkyl disulfides. Others use diethanol amine solution to remove the sulfur compounds. Copper sulfate in HCl is another sweetening agent. From this, copper sulfide or mercaptide is formed and removed from the gasoline, then regenerated by addition of air to the waste slurry.

GASOLINE SPECIFICATIONS

The chemist is also valuable in the final blending of gasoline to make the required marketing specifications. A wise chemist knows how much of each type of gasoline to blend to make the best gasoline with the least amount of TEL (tetraethyl lead). The TEL added increases the octane of various gasolines differently. Gasolines with high TEL susceptibility may be raised 10 to 15 octane numbers by the addition of one cc. per gallon; others with low susceptibility may only be raised from one to two octane; and surprisingly, we have found that mixtures of two different types of gasoline stock will have also far greater or far less susceptibility than expected from the parent blending stocks. The chemist is expected to use these factors when he makes his blends of the gasolines for today's cars. Since TEL is quite expensive and is

often added to tank mixes by the ton it behooves the chemist to prepare the most favorable blends.

Octane rating is not the only important specification point of gasoline. Equally important from a performance standpoint are the following items:

(1) *Volatility.* How easily does it start a car, or will it cause vapor lock? Volatility is adjusted seasonally by the addition of butane or casinghead to the correct range.

(2) *Gum Content.* Will the carburetor or rings foul because of high gum? Gum-forming tendency is corrected by the addition of inhibitors to the gasoline to reduce the rate of autooxidation.

(3) *B.t.u. Content or Power Available.* This is regulated by the general distillation range. Good mileage gasolines are those with a large amount of liquid in the upper end of the gasoline boiling range (275–400°F.).

(4) *Sulfur Content.* Is the gasoline odorous or pleasant-smelling? Will it be corrosive?

If the refinery chemist can meet all these specifications in the correct way, he has saved his company money and earned his salary.

The chemist, with all of his tools, is able to blend and prepare high-octane gasoline for sale, including tax, at a price two cents less per gallon than that sold in 1920. In addition, today's gasoline is at least 50 per cent better than the gasoline prepared 30 years ago. Did you know that the tax on gasoline averages over 35 per cent of its value? It is taxed higher in proportion than such luxuries as furs and jewelry, and is exceeded in tax rate only by tobacco and alcohol. The average national tax per gallon on gasoline was 7.32 cents in 1952; in 1920 it was only 0.09 cent.

OILS

The usual phase of refining is to produce gasoline, distillates, and fuel oils. Some refineries go a step further and, by processing special crudes, make base stocks for lubricating oils. The special processes involved are as numerous and as technical as those used in preparing gasoline. In lubricating oils we must produce an "oiliness" which is not present in naturally-occurring petroleum oils. We try to promote an oil plating, or film-forming characteristics. We must keep the oil on the anti-acid side; yet it must not be too basic or foaming results and our attempts to add detergents would be useless. We must develop an oil that is free-flowing in cold weather and yet retains body or viscosity under warm operating conditions.

No two lubricating oils are exactly the same. Each is developed for specific purposes. Each company has its own chemicals and additives in the oils. Most oils today are excellent.

The chemist, in blending these oils, is indeed a busy man in the industry. He must, in addition to the gasoline blending and the lubricating-oil preparation, handle such things as cold tests on diesel fuels, viscosity on heavy fuel oils, burning qualities of kerosenes, melting points of waxes, the saponification of greases, etc.

PETROCHEMICALS

We have a glamor child in the petroleum industry. It has been designated "petrochem." It is intended to mean the chemical industry grown up from petroleum sources and by-products. In many cases the petrochemicals produced as by-products of processes are as valuable as the main product. The field of petrochemistry is only in its infancy, and much is expected from it within the next few years.

Already important petrochemicals are on the market, and some have completely outstripped the coal-tar chemicals in price economy and sales volume. Important petrochemicals include ethylene glycol, alcohols, butadiene, synthetic rubber, detergents, resins, fertilizers, plastics, textiles, insecticides, solvents, ketones, ether, esters, and phenols.

In 1953 the volume of organic chemicals derived from petroleum amounted to an estimated 28.9 billion pounds. This was about 25 per cent of all chemicals made in the United States. Three billion dollars is invested in petroleum chemical facilities, or two and one-half times the amount invested at the end of World War II. This is a husky infant in our midst, which we expect to grow up to be a heavyweight.

INFORMATION SERVICE

For many years the oil industry had been a laggard in tooting its own horn. Recently the American Petroleum Institute, in conjunction with leaders in the industry, established the Oil Industry Information Committee. This committee supplies and furnishes all kinds of information about the industry to anyone who wants to know more about us.

Last spring it launched the OIIC School Plan, after three years of trial and preparation. The plan is eventually to carry the oil industry message to ten million school children. The committee has prepared booklets, pamphlets, movies, talks, textbooks, charts, and maps for teachers. The material is free of charge. Included are "The Chemistry of Petroleum," "The Physics of Petroleum," "Petroleum in our Age of Science," "The Conservation of Petroleum," and "Petroleum in our Modern Society." Each of these is a separate booklet which can fit inside a student's notebook.

For teachers, we have "The Teacher's Handbook and Work Supplement," "Careers in Petroleum," wall chart and the key to the chart, a catalogue on movies about oil, a leaflet on programs about oil, and two strip films with the story of each. These materials are available from your nearest OIIC office or from the American Petroleum Institute, 50 West 50th Street, New York 20, N. Y.

FRIEDLIEB FERDINAND RUNGE: A FORGOTTEN CHEMIST OF THE NINETEENTH CENTURY

BERTHOLD ANFT
Berlin, Germany
(Translated by Ralph E. Oesper)

Too little attention has been given to the life and achievements of F. F. Runge. Even the histories of chemistry mention him casually if at all, and frequently the accounts are inaccurate. The author first became interested in this exceptional man during a course on the history of chemistry, and over the years he collected publications and studied files of documents that have shed much light on the life and times of a brilliant observer and capable practical chemist. Unfortunately most of this unique collection was destroyed during the last war, but most of the findings had already been put into permanent form in a dissertation submitted to the University of Berlin.[1] Besides the ordinary sources, the author examined the minutes of the Philosophical Faculty of the University of Berlin, the patent files, and the secret government files. Particularly valuable information was gleaned from the mass of documents preserved by the Prussian State Bank at Berlin.

This paper makes no attempt to cover the manifold activities of Runge. Its purpose is to introduce this worthy career to the readers of THIS JOURNAL in the hope that this forgotten chemist will be more properly appreciated. Besides a variety of minor but valuable discoveries, Runge discovered independently (though not always before others): caffein, quinine, aniline, phenol, pyrrole, and rosolic acid. He was the first to prepare a coal-tar dye. He also should be credited with being the first to use impregnated test papers in a scientific fashion and his extensive studies and publications entitle him to consideration as the founder of paper chromatography.

YOUTH AND APPRENTICESHIP (1794–1816)

Friedlieb Ferdinand Runge was born on February 8, 1794 (not 1795, as sometimes given) at Billwärder near Hamburg. He was the third of seven children; his father was a pastor.[2] The prosperity of the Hamburg district was wiped out by the Continental Blockade and the occupation by the French, a period almost without break from 1806 to 1814. The family had hard sledding and there could be no thought of sending the children to anything beyond the local elementary school.

At 15, Runge was apprenticed to his uncle at the Ratsapotheke in Lübeck. At this early stage he already exhibited his remarkable powers of observation. While preparing a medicine, in which the juice of hyoscyamus was to be dissolved in water, a drop of the liquid spattered into his eye. After a time he noticed that the pupil was dilated and that the sight was weakened. In the literature he is listed as the sixth discoverer of the mydriatic action of belladonna.

STUDENT YEARS AT BERLIN, GÖTTINGEN, JENA

In 1816 Runge went to Berlin to study medicine. This choice was an obvious one in view of his interest in natural science. After two years he transferred to Göttingen. He attended the chemistry lectures by Stromeyer, who had organized one of the earliest teaching laboratories in Germany.[3] Here Runge received the first stimulations for his subsequent chemical investigations. After one semester he transferred to Jena where he finished his medical course with a dissertation on belladonna (1819). This study, which was based on the Lübeck observation, dealt with the discovery of the toxic actions of atropin occurring in three plant species: deadly nightshade, thornapple, and henbane. As reagent he employed the eye of a young cat. This *in vivo* test was adopted not only in forensic medicine but also as a general test for atropin-bearing substances.

At Jena, Runge studied analytical chemistry under J. W. Döbereiner,[4] the chemical advisor of Goethe. Runge was now devoting all of his time and energy to chemical researches, especially plant chemistry, and Döbereiner did not delay in telling Goethe about Runge's discoveries, particularly the ability to dilate the cat eye simply and at will. Goethe wanted to see the experiment and an audience was arranged. Wearing a borrowed frock coat and a formal hat, Runge set out of Weimar, his cat under his arm. In the Jena market place he was soon surrounded by fellow students, who naturally made sport of his costume and companion. To them he was affectionately known as Dr. Gift (Poison) because of his known predilection for dabbling with toxic materials. They were properly

[1] ANFT, B., "Abhandlung zur Geschichte der Medizin und der Naturwissenschaften," Heft 23; later issued as the brochure: "F. F. Runge—sein Leben und sein Werk," Verlag Emil Ebering, Berlin, **1937**. Other publications dealing in some detail with Runge are: SCHELENZ, H., *Chemiker Zeitung*, **30**, 807 (1906); *Pharmazeutische Centralhalle*, **1907**, pp. 301, 342; **1906**, p. 751; *Chemiker Zeitung*, **32**, 268 (1908). REHBERG, M., "F. F. Runge, der Entdecker der Teerfarben," Oranienburg, **1935**. KRÄNZLEIN, G., *Z. angew. Chem.*, **48**, 1 (1935).

[2] The present parsonage at Billwärder was marked by a memorial plaque October 10, 1936, by the Hamburg Section of the Verein deutscher Chemiker.

[3] LOCKEMANN, G., AND R. E. OESPER, J. CHEM. EDUC., **30**, 202 (1953).

[4] PRANDTL, W., J. CHEM. EDUC., **27**, 176 (1950).

awed when he explained his destination. Goethe was greatly pleased with the demonstration; he showed much interest in Runge's current researches, and at the close of the interview presented him with a packet of mocha coffee beans, suggesting that these rather rare vegetable products might well yield interesting chemical results. Runge analyzed the coffee beans and in this same year discovered caffein in them.

Runge's visit to Goethe was a brilliant and memorable event in his scientific career, since it led to a notable advance in purine chemistry. To the end of his life he enjoyed telling of this outstanding incident of his early days.

Still another important discovery marked his Jena period. His studies of cinchona bark led to a basic constituent, namely his "China base." He announced his discovery in the periodical *Isis*, which was edited by the naturalist Lorenz Oken, and again a year later in his own *Neueste phytochemische Entdeckungen zur Begründung einer wissenschaftlichen Phytochemie*.[5] Almost all the histories credit the discovery of quinine to the French team, Pelletier and Caventou. A comparison of the properties of Runge's "Chinabasis" with those of Pelletier and Caventou's "Chinin" shows conclusively that they were identical. On the basis of these studies in the history of the discovery of the alkaloid, Runge should be given the priority since he reported quinine as early as 1819—a year before the French workers.

A similar situation arose regarding the priority in the discovery of madder purple (purpurin). It has been stated that purpurin and alizarin were discovered in 1826 by Robiquet and Colin. Actually, Runge discovered purpurin four years earlier. The files regarding patents in the Prussian State Archives prove that Runge applied for a patent in 1822; the application is in his own handwriting. The desired patent was granted by the Ministry of Commerce on February 15, 1823. It is regrettable that he missed the madder red (alizarin); otherwise he would have earned the credit for this important discovery also.

The discovery of caffein, quinine, purpurin, and the mydriatic action of belladonna—discoveries which he accomplished while still a student and in his formative scientific years—put him among the brilliant chemical workers of the nineteenth century. He constructed his youthful scientific ideas entirely within the spirit of natural philosophy; yet he conducted his chemical researches with due regard to actual practice, and he always stood firmly on the soil of reality. His discoveries in what are ordinarily the romantic years in a young man's life are ample proof of his practical bent.

Runge wanted to become a professor, so in 1819 he went back to the university to habilitate as *Privatdozent*. For all who wished to belong to the philosophical faculty it was necessary first to acquire the Ph.D. degree. This regulation made Runge's career as an advanced student most difficult, since he was practically without funds. He probably received aid from student friends, especially his countryman J. F. Poggendorff, later professor of physics and well known editor of the *Annalen für Physik und Chemie*. Another friend in this time of need was the poet and philologist August Heinrich Hoffmann (better known as Hoffmann von Fallersleben) whose close association with Runge lasted through many years. The experimental research for the degree dealt with indigo and its combination with metal salts and oxides.[6]

The university records give interesting insights into Runge's petitions and doctorate examination. The oral examination, on June 14, 1822, revealed that the candidate was not able to respond in Latin to the question put to him in that language by Weiss, for the simple reason that he did not understand the question. He had attended only the elementary school and later his experimental researches had left him no time for subjects like Latin. According to von Fallersleben this must have been one of the most comic examinations ever witnessed at a German university. As a true German, Runge had a low opinion of the use of

Runge Trying His Synthetic Wine

foreign languages in German countries, but was confronted here with the tradition that the thesis had to be defended in Latin. He spoke brilliantly, throwing phrases around freely, and when he had no idea what he ought to say he took refuge in some familiar but irrelevant proverb: *Practica est multiplex* (Practice is varied); *Post nubila Phoebus* (After the clouds, the sun); *Errare est humanum* (To err is human); *Plenus venter non studet libenter* (A full stomach does not care for study).

He had similar lack of success with Lichtenstein, who questioned him on general physiology and zoology. In chemistry he did well with Hermbstadt. The renowned philosopher Hegel closed the examination with

[5] This periodical was designed to be a collecting point for all discoveries in plant chemistry. Unfortunately, this ambitious project collapsed after only two issues. Runge probably bore the printing costs himself.

[6] "De pigmento Indico ejusque connubiis cum metallorum non nullorum oxydis," Dissertation inaug. Berolini, 1822.

questions on matters of form of scientific perception, taking his cue from the candidate's publication, "Materialien zur Phytologie," which he displayed to the faculty. Hegel noted that the candidate lacked certain concepts regarding the scientific character of perception and hoped that he would endeavor to remedy this situation. The vote was favorable because of the candidate's "demonstrated knowledge, both in the examination and his published work, of his major field, chemistry, and because of his diligence and many skilful observations and combinations." His was the second doctorate granted by the philosophical faculty since the founding of the university in 1810. (The first was awarded in 1820 to Gustav Rose, who later became famous as a mineralogist.) After a year at Berlin the young *Privatdozent* went to Breslau but soon decided to broaden his outlook.

THE EUROPEAN JOURNEY (1823–26)

Originally planned for one year, Runge's European trip lasted from October, 1823, to April, 1826. His main goal was Paris, at that time the scientific center of the world. Here he came into contact with his countrymen Alexander von Humboldt and Justus Liebig.[7] Runge worked in the laboratory of J. B. Quesneville, who had a factory for the manufacture of pharmaceutical-chemical products. He gave Runge the task of isolating the narcotic principle of belladonna from 200 pounds of deadly nightshade leaves. Liebig was working with Gay-Lussac on fulminates.

It is regrettable that, with the exception of two letters, Runge left no reports or notes about this extended stay abroad. In a letter to the Ministry he reports that he had visited the excellent chemical factories in France and Switzerland, and that through the kind offices of Alexander von Humboldt he had been permitted to see the chemical works in England which ordinarily were not open to visitors. The other letter, undated, was addressed to Liebig. It was written "on the point of leaving for Switzerland and Italy." He sends his best wishes on the new appointment to a professorship at Giessen and proudly relates that his paper on dioecia and scabiosa would be read to the Institute, and that Humboldt had given a very favorable opinion of it. He continues:

> Recently Rose and I were at the Gay-Lussac's for midday meal. I was given the seat of honor between Madame and Mademoiselle Gay-Lussac. You are highly regarded by Madame Gay-Lussac also. We spoke a lot about you and when I translated your name ("liebe ich: est ce que j'aime") they were much amused.

The letter is jokingly addressed to "Freund Liebich." The two young men went their separate ways and the years did not bring them together again except occasionally at scientific conventions. They differed too much in personal character and in ambition to arrive at positions of eminence ever to have become intimate, long-standing friends.

Runge greatly admired the high development of agriculture which he saw on this trip in England and Holland. In these countries he received the impetus to occupy himself later with agricultural chemistry and attempts to produce an artificial fertilizer.

THE BRESLAU YEARS

After his long absence from Germany, Runge returned to the University of Breslau as *Privatdozent*. One of the attractions was Hoffmann von Fallersleben, who had become curator of the university library the year before. Runge joined the Silesian Society of National Culture and delivered a series of lectures on chemistry before the science section of this organization. He also continued his laboratory studies with great ardor, composed papers on various subjects, and wrote textbooks. His "Grundlehren der Chemie für Jedermann: besonders für Ärzte, Apotheker, Landwirte, Fabrikanten und Gewerbetreibende" (1830; third edition, 1843) shows his competence in writing in a popular style. He did not believe that science lectures and publications should be above the comprehension of the masses because of the use of fine spun theories and professional jargon. Instead, he advocated the use of simple language and numerous illustrations taken from daily life. Science could thus be introduced into all sorts of craft operations and made of value to everyone. He had a natural interest in practical chemistry and was well aware of the fact that technical chemistry was almost entirely omitted from chemical instruction, largely because of the miserable teaching facilities then available.

Runge's ideas and endeavors are likewise visible in the reports of the Silesian Society for National Culture. In this organization he advertized (1828) a course dealing with technical chemistry, but the lack of a laboratory was a terrific handicap. The next year he was authorized to rent space in which a laboratory could be installed. Part of the funds were provided by the government authorities and characteristically he added what he could from his meager resources. He came to have less and less to do with the university. Actually, he felt out of place in professorial circles because the elegant manners prevailing there were not in harmony with his gruff approach and blunt dealings with his fellowmen. He sought the company of those who were of his own kind.

Runge was an enthusiastic attendant at scientific meetings in other cities and reported his new findings, particularly those issuing from the continuation of his phytochemical researches. He found that copper oxide is a good reagent for plant acids. Among other things he investigated tanning agents and flower pigments. During the terrible cholera epidemic of 1831 he was made head of the disinfecting station and successfully introduced chlorine in place of acetic acid and sulfur dioxide, which were then in general use.

Even at this early period he was working on reactions conducted on absorbent paper, and believed that his results could be applied in the manufacture of government documents and particularly paper money. He got in touch with the authorities in Berlin, who invited

[7] OESPER, R., J. CHEM. EDUC., **4**, 1461 (1927).

him to come at once, expenses paid plus a per diem allowance of three talers. He was urged to keep this visit and its reason a secret. He demonstrated his process, arguing that it was superior to the usual water marking of paper. However, nothing came of his proposals.

TECHNICAL DIRECTOR AT ORANIENBURG

Although Runge had been promoted to extraordinary professor of technical chemistry in 1828, he found that the conditions were unfavorable to the development of his practical ideas. Finally, in 1831 he moved to Berlin and put an end to his academic career. After the usual negotiations, he was offered a position, in 1832, in the chemical works at Oranienburg, a small town near Berlin. In 1829 the great Berzelius had said that he had not seen the equal of this establishment in its comprehensive accomplishments in either France or England. The business had been conducted for many years by its owner, G. F. A. Hempel, in the old palace which had been sold by the Crown in 1802 and converted into a cotton mill. After many vicissitudes, chemical manufacturing had been started in this group of buildings and at the time Runge came on the scene the chief products were sal ammoniac, yellow prussiate of potash, Berlin and Paris blue, chrome yellow, Glauber salt, soda, sulfuric acid, and soda soap.

Hempel had been in financial trouble and in 1832 the chemical works was taken over by the Königliche Seehandlungs Societät to protect its investment, and the name was changed to Chemische Produkten-Fabrik zu Oranienburg. Hempel stayed on as "owner," Ernst Eduard Cochius was installed as business manager, and Runge became Hempel's chemical colleague. The principal source of income was concentrated sulfuric acid, but the administration was aware of the possibility that new diversified activities might prove profitable.

Runge now began the most fruitful period of his life. He was given somewhat of a free hand, and building on his previous interests and researches he began to study the field of color chemistry. Within two years he made the notable discoveries which place his name among the chemical immortals. By distilling the coal tar that was all over the premises as a waste product from the gas liquor (from the Berlin gas works), and treating it with hydrochloric acid to prepare sal ammoniac, he eventually discovered phenol, aniline, pyrrole, rosolic acid, and a mixture which later proved to be made up of quinoline, isoquinoline, and quinaldine. He was the first to produce aniline blue, an accomplishment of the highest historical importance since this was the earliest preparation of an artificial organic coloring matter from a distillation product of coal tar. He discovered other color reactions of aniline, such as the yellowing of a pine splint. He was the first to prepare aniline black and its important oxidation product emeraldine. Details of these achievements are given below.

Oranienburg Palace, Converted to Chemical Purposes

Runge made his great discoveries here while in the employ of Chemische Produkten Fabrik.

DISCOVERY OF COAL-TAR PRODUCTS

Runge began by trying the solubility of the tar in water, alcohol, and ether. Then he tested its reaction toward acids and bases. No distinct results were observed. Consequently he decided to employ more drastic attacks, notably dry distillation at various temperatures. He used a retort and a sand bath. The volatile distillates were collected in a flask. The liquid in the receiver was an oily material with a penetrating odor. Preliminary trials showed that it could be separated into two fractions of differing volatilities. This separation was made by adding water and then distilling. A light volatile oil was collected in the receiver while the remainder, about one-half the original sample, remained in the retort as a thick brown oil.

The light oil that had passed over was studied first. When shaken with milk of lime, an acidic constituent dissolved and formed a clear solution. Runge called this substance "carbolic acid." Addition of an excess of hydrochloric acid to the aqueous solution in lime-water produced oily drops that had a distinct odor reminiscent of *castoreum*. The substance dissolved to some extent in water. Runge regarded its antiseptic power as its most striking characteristic.

When he boiled down a solution of the lime salt, Runge found that a dark red powder separated on the walls of the flask. This product contained a dyestuff, which he named "rosolic acid" because of the color that could be obtained with it. At the same time, he found the accompanying brown dyestuff that he called "brunolic acid" because of the sepia shades it imparted to cloth.

Runge next tried the action of sulfuric acid on his two original products. The light oil was shaken with the acid, the layers were separated, and the acidic water solution was heated to drive off the volatile odorous principles. The residual solution was almost devoid of smell and had no decided color. However, addition

of caustic potash showed that the sulfuric acid had extracted several materials from the light oil. A penetrating odor was given off by the alkalized solution and when the latter was heated this smelly substance passed into the receiver, along with water, and appeared as a colorless oil. This formed odorless salts with acids, and all of these salts had the remarkable property of developing an odor resembling phosphorus and hydrocyanic acid when they came into contact with the moist skin. Runge named this material "leucol" or "white oil." In this study he accidentally spilled a little of the sulfuric acid solution on several kinds of wood and textiles. To his amazement, a pine splint was made yellow, whereas other woods and the textiles were not colored.

He also made the important observation that when a solution of chloride of lime was shaken with the light coal-tar oil of the second distillation, a dark, blue-violet color developed. Consequently, free chlorine, which heretofore had always been found to destroy organic coloring matters, acted here to produce a colored product. Since his recently discovered leucol did not show these actions and changes, Runge concluded that he was dealing with still another new substance, which he proceeded to separate and free of leucol. It had an oily consistency; it likewise formed colorless salts with acids, but they imparted no odor to moist skin. However, when mixed with a solution of chloride of lime it always yielded a violet-blue color. Accordingly, he named this material "kyanol" or "blue oil" and made an extensive study of its various remarkable properties. He found, first of all, its marked coloring properties, such as its action on pine. One gram of "kyanol" (cyanol) was sufficient to stain 20 square feet of pine. Still more notable were the changes he observed when he treated it with various chemicals. Violet, blue, and reds appeared, depending on whether he used chlorine, chromic acid, nitric acid, copper chloride, gold chloride, etc.

In the original report, which he sent to the 1833 convention of the Naturforscher und Ärzte in Breslau, Runge told of the first two products: carbolic acid and rosolic acid. The later published accounts[8] dealt with additional findings regarding the distillation of coal tar, and comprehensively described three bases and three acids. These basic products were kyanol or blauöl, pyrrol or rotöl, and leucol or weissöl. The acidic materials were carbolic acid or kohlenölsäure, rosolic acid or rosaölsäure, brunolic acid or brunaölsäure. When naming these materials, Runge obviously was guided by the characteristic color reactions they displayed with various substances. The names were constructed from *oleum* and the Greek or Latin terms for the respective colors.

With respect to the individual products, his findings can be summarized:

Carbolic Acid. He subjected this material to the most varied reagents and demonstrated its characteristic properties. By the action of metallic potassium he obtained hydrogen and potassium carbolate, a colorless crystalline mass. He described its "decay staying action," *i. e.*, its ability to preserve animal materials, and its protection of wood impregnated with it. He did not give its ultimate composition, which was established in 1841 by Laurent. The latter had likewise isolated it by distilling coal tar, and called it "acide phenique" or "hydrate de phenyl."[9] Laurent stated that the properties of his compound showed many similarities to the Runge carbolic acid, as proved by a comparison of their respective findings. Because of the high boiling point of carbolic acid (197.5°C.) and of phenyl hydrate (188°C.), Laurent concluded that Runge's carbolic acid was impure phenyl hydrate. (The boiling point of pure phenol is 180°C. Runge's product is now known to have contained cresols.) The next year Gerhardt distilled a mixture of salicylic acid and lime and obtained a colorless oil which had all of the properties of Laurent's phenyl hydrate. Gerhardt called this oil "phenol" because this name corresponded to "anysol," which had been coined by Cahours for the decomposition product of anisic acid. Since 1859 this acidic compound has been made on a large scale; its use as an antiseptic, particularly in medicine and surgery, was due primarily to Lister (1867). This indispensable material was Runge's discovery, a chemical feat that is universally credited to him.

Rosolic and Brunolic Acid. These two other acidic products need but little comment. Runge emphasized that rosolic acid behaves like a real pigment and with suitable mordants it yields colors whose beauty compares most favorably with those derived from safflower, cochineal, and madder. Ladenburg believed that the discovery of rosolic acid should be credited to Kolbe and Schmidt, and simultaneously to Persoz, but the 1834 paper by Runge establishes definitely that he discovered this compound and its red lakes. Nevertheless, Persoz took out a French patent for his alleged discovery on July 21, 1862.

Runge stated that brunolic acid accompanies rosolic acid. He described it as similar to asphalt in appearance, and also reported that its compounds, in contrast to those of rosolic acid, are not soluble. This material has not been identified by modern chemists.

Leucol or Weissöl. This was subsequently found to represent a mixture of quinoline, isoquinoline, and quinaldine. The discovery of this fact is due to A. W. Hofmann, who was working in Liebig's laboratory in Giessen at that time.[10]

Pyrrole or Rotöl. Runge described the properties of this material in his first 1834 paper and went into more details the next year. In 1850 Anderson separated this compound from bone oil and confirmed the reaction that it gives a purple-red color with a pine splint. In 1858 he stated that he was retaining the name given to it by Runge because of characteristic reaction, even though the term pyrrole did not conform to the prin-

[8] RUNGE, F. F., *Pogg. Ann.*, **31**, 65, 513 (1834); **32**, 308, 328 (1834).

[9] LAURENT, A., *Ann. pharm.*, **43**, 200 (1842).

[10] HOFMANN, A. W., *Ann.*, **53**, 427 (1845).

ciples usually followed in naming organic compounds.[11]

Kyanol and the First Synthetic Coal-tar Dyestuff. The blue developed by the action of a solution of chloride of lime on kyanol was proposed as an important reagent for this organic compound. This reaction is important in the history of tar dyes because it is the earliest example of an artificial coloring matter produced from a distillation product of coal tar. Runge used other color reactions of kyanol. For instance, he streaked a porcelain plate with gold chloride, heated the plate to around 100°C., and then added a drop of kyanol. A purple spot appeared, which quickly developed blue edges, and turned blue-green when baked to dryness. The following reactions led him to important results:

> Kyanol nitrate shows very singular reactions when it reacts with hydrochloric acid and copper oxide. If a porcelain plate heated to 100°C. is streaked with copper chloride and, after it has dried, a drop of kyanol nitrate solution is placed on it, a dark green fleck appears at this place.... A drop of kyanol chloride solution placed on a heated porcelain plate that has been streaked with potassium bichromate produces a dark black fleck. If the same salt is printed on cotton that has been colored yellow by lead chromate, green patterns appear within 12 hours. These are black if the solution of kyanol chloride is concentrated. Both remain unaltered when treated with water.

Thus Runge described the first preparation of aniline black and one of its most important oxidation products, emeraldine.

Some historians have stated that Fritzsche, in 1840, found that the green or black precipitate which results from the action of chromic acid on solutions of aniline salts is characteristic of this material. As was pointed out above, Runge had observed this reaction several years earlier. In 1863 John Lightfoot obtained an English patent for producing aniline black on textiles. Actually, Runge had done this some 30 years previously. The story of the young William Henry Perkin (1838–1907), who was working in W. A. Hofmann's laboratory in the Royal College of Chemistry in London, is too well known to be given in detail here. He was attempting to prepare quinine by oxidation of allyltoluidine, but had no success. He then tried aniline sulfate. The black precipitate yielded the violet coloring material that he called "aniline purple," and which later became known as mauvein. The patent for its preparation was granted in 1856. It should be remembered that Runge produced a blue material as early as 1833 by the action of bleaching powder on aniline and thus was the earliest discoverer of synthetic tar dyes. Runge must be credited with not only the discovery, but also with the idea of creating a coal-tar dye industry. The reasons why his suggestions failed are given later.

The fiftieth anniversary of the beginning of this great industry was celebrated with due ceremony on February 26, 1906, at the Royal Institution in London. Honors were showered on Perkin, but Runge was forgotten even in his own country. On June 19, 1906, the German Chemical Society awarded its highest award, the Hofmann medal, to Perkin, and the accompanying certificate stated that the medal was being conferred "in recognition of outstanding investigations in the organic field and especially for the founding of the tar dye industry." Emil Fischer, then president of the Chemical Society, delivered the medal in person and held a lengthy eulogy on the achievements of Perkin. Apparently not one of the German chemists took note of Runge and the discoveries he had made in 1833.

Runge himself went on to other fields. About ten years later A. W. Hofmann, who was then assistant to Liebig, followed up Runge's interesting findings. He prepared the same products but considerably shortened the tedious distillation by using new methods. He became particularly interested in kyanol. A similar basic oil had been prepared in 1840 by Fritzsche by distillation of indigo with caustic potash. He called it "anilin" (from the Portuguese *anil*, which means "indigo"). That same year Erdmann studied this substance and came to the conclusion that it was the same as "crystallin," which Unverdorben had reported in 1826 from the distillation of indigo. In 1842 Zinin was studying the action of ammonium sulfide on the compounds of nitrogen dioxide with several hydrocarbons and obtained a number of organic bases. One of these, which Zinin prepared from nitrobenzene and named "benzidam," was recognized by Fritzsche as identical with his anilin. Hofmann suspected that all of these materials were related and by ultimate analyses demonstrated that in fact crystallin, anilin, benzidam, and kyanol all had the composition $C_{12}H_{14}N_2$. Further studies by Hofmann showed them to be identical and he proposed that the name crystallin be retained for this organic base.[12] The name kyanol should be dropped, he believed, because it was a hybrid (Greek *kyanos* and Latin *oleum*), and furthermore the Greek adjective (blue) is misleading in this case. The name aniline was accepted, however, on the authority of Berzelius who argued that "crystalline" was too general a characteristic. In any event, Runge was undoubtedly one of the independent discoverers of this extremely important compound and pointed the way to some of its possibilities.

Hofmann confirmed Runge's findings. The latter, many years later,[13] praised Hofmann's study of kyanol and stated:

> The discovery in question has recently taken precisely the course that it had to take, and it has led to tremendous success. Various workers have already tried to prepare kyanol by other processes and have given it the names "anilin" and "benzidam." The Englishman Perkin succeeded in preparing the compound itself and its dyes with the aid of nitric acid and several reagents, in such large amounts that these materials have become articles of commerce. Today, at the London Exposition, Perkin is displaying a cylindrical container 50 cm. high and 23 cm. wide, filled

[11] ANDERSON, TH., *Ann. pharm.*, **80**, 44 (1851); **105**, 335 (1858).

[12] HOFMANN, A. W., *Ann.*, **45**, 250 (1843); **47**, 37 (1843). See also DARMSTÄDTER, L., *Chem. Eng. News*, Oct. 10, **1927**; SCHELENZ, H., *Z. angew. Chem.*, **34**, 31 (1921); SCHLENK, O., *ibid.*, **39**, 757 (1926).

[13] RUNGE, F. F., *Monit. sci., Paris*, **5**, 533 (1863).

with kyanol dyes, which were obtained by treatment of 2000 tons of coal. This is enough coloring matter to dye 500 kilometers of silk according to a newspaper report, an estimate which seems not exaggerated if one recalls the coloring power of kyanol observed by me on pine wood.

These are the extents to which this discovery has gone, whose first recognition, disclosed by me 28 years ago, was so misunderstood and put into such a bad light.

My discoveries have been remembered by the Board of the Exposition and they have unanimously awarded to me their medal of merit.

It is indeed pleasant that this news of my successes has come to me while I am still in the land of the living.

This historical review paper on "The colors derived from tar oil" was written when Runge was 69. Shortly before his death, and after he had witnessed the triumphal realization of the coal-tar industry he had predicted in vain some three decades earlier, he wrote: "All this has grown from the tiny beginning which first saw the light of day under my eyes 34 years ago."

SPOT TESTS AND PAPER CHROMATOGRAPHY

Runge was one of the important pioneers in the use of absorbent papers as the seat of chemical reactions. In a sense, he can be regarded as the creator of paper chromatography. This historical fact has recently been discussed in considerable detail[14] and deserves wider recognition.

Runge's Residence (1856–67) in Oranienburg

All of the accounts of the development of paper chromatography, as well as the comprehensive texts on this procedure and the related field of spot testing, state that C. F. Schönbein and F. Goppelsroeder were primarily responsible for the creation of paper chromatography in that the principles underlying this technique are taken to be identical with those of capillary analysis, as developed by them from 1861 on. Feigl states that the earliest spot reaction on impregnated paper was reported by Schiff in 1859. However, these assumptions are incorrect.

Three historical periods of chromatography can be distinguished: empirical, scientific, and technological (still in its beginning stage). The historical boundaries between the first two periods are characterized by Runge's studies, but his researches in this field have been seemingly forgotten or overlooked. From 1850 he systematically described several essential particular features of paper chromatography.

Runge's priority is not impaired by the fact that as early as 1844 Carlo Matteucci[15] incidentally cited as an example the fact that a drop of chocolate placed on filter paper produces a dark stain surrounded by a lighter zone. Of course, any discussion of the creation of the chromatographic method must include the studies of M. Tswett.[16] In the light of the published evidence, Tswett can certainly not be credited with the invention of chromatography as has long been assumed and is still believed by many.

When Runge developed his system of scientific paper chromatography he was strongly influenced by the prevailing practice of the dyestuff industry. Consequently, the early stage of paper chromatography was closely related to empirical procedures that since early times had been widely used for testing commercial coloring matters, pigments, and the like. Color reactions employing spot tests on impregnated or non-impregnated textiles or paper were known methods when Runge in 1822 evinced interest in the preparation and determination of dyes and pigments in his Berlin dissertation dealing with indigo and its combinations with metals and oxides.

Later, in his intensive investigation of aniline, he sought for an accurate method of determining the strength of bleaching solutions. Whereas leucol (quinoline) gave no blue color reaction, the color was instantly formed when a solution of bleaching powder came in contact with aniline. This of course is the famous blueing of aniline by chlorine. In the first volume of his "Farbenchemie,"[17] Runge outlines a procedure for measuring the strength of bleaching powder solutions by bringing a drop of the solution to a piece of dyed cotton goods. To test for free chlorine, paper was impregnated with starch and potassium iodide, as described in Volume 2 of his "Farbenchemie." When the paper was spotted with bleaching solution, a blue fleck appeared because of the liberation of iodine and its reaction with the starch. This is probably the earliest scientifically checked authentic spot reaction with impregnated paper. It antedates Schiff's test for uric acid on silver carbonate paper by 25 years.[18]

In 1850 Runge put out two books which may be viewed as the earliest known works on paper chromatography. One is Volume 3 of his "Farbenchemie," the

[14] WEIL, H., AND T. J. WILLIAMS, "Die Naturwissenschaften," **1953**, pp. 1–7

[15] MATTEUCCI, C., "Lectures on the Physical Phenomena of Living Beings," London, **1847**.

[16] For reviews see *Ber. deut. Ges. Bot.*, **24**, 384 (1906); *Trav. Soc. Naturalistes Kazan*, **35**, 268 (1901).

[17] RUNGE, F. F., "Farbenchemie: Teil 1: Die Kunst zu farben gegründet auf das chemische Verhalten der Baumwollfaser zu den Salzen und Saüren. Lehrbuch der praktischen Baumwollfärberei," Berlin; **1834**; "Teil 2: Die Kunst zu drucken," **1842**; "Teil 3: Die Kunst der Farbenbereitung," **1850**.

[18] SCHIFF, H., *Ann.*, **109**, 67 (1859). See also FEIGL, F., "Specific, Selective and Sensitive Reactions," New York, **1949**, p. 582.

other his "Musterbilder,"[19] a contribution to color chemistry. The latter contains 120 original pictures, whose wondrous color quality is still to be seen in the copy at the British Museum. The 1855 continuation is now very rare. There are known copies at the Deutsches Museum in Munich, in the Senckenbergsche Bibliothek in Frankfurt, and in private possession in Chicago.

The scientific foundation of Runge's work cannot be doubted, and the fact remains that he created scientific paper chromatography and perhaps scientific spot-reaction technique more than a century ago.

An interesting fact in this connection is that in these "pattern pictures," which he called his "chemical coat of arms," he saw the possibility of preparing the paper for state documents and paper money.

THE MACHINATIONS OF COCHIUS

In view of the phenomenal and rapid development of the coal-tar industry, it is logical to ask why his employers paid no attention to Runge's suggestions and discouraged him from perfecting methods of preparing large quantities of his newly found materials. Had they not done so, there is every reason to believe that the industry would have been built up in Germany before Perkin came on the scene and the history of chemical technology both in Britain and on the Continent might have been radically different from what actually occurred. Runge had a great sense of the practical side of chemistry and his ardent enthusiasm would have surely supplemented his innate brilliance as a chemical discoverer. All that was needed was an order (or permission) from his superiors, and he undoubtedly would have plunged into the new field of endeavor like one possessed.

However, precisely the opposite occurred. In his "Hauswirtschaftliche Briefe" Runge wrote:

> Brakes were applied against all the proposals I made to the Seehandlung; they were met with an opposing spirit and an unwillingness to undertake anything new. The responses were invariably negative or I received no answer at all, because my opponent, the higher-up to whom the matters were referred, was very clever in presenting my suggestions as being not yet suited to the times or as offering too little prospect of yielding a profit. Since I myself had no doubts about the technical importance of the matter, I suggested to the Königliche Seehandlung, whose chemical works in Oranienburg were then being directed by me, that all of the substances specified by me be prepared in large amounts by treatment of the tar oil. All my efforts failed because of the professional opinion of some unknown official of the firm.

Runge, thoroughly honest, and naive besides, had assumed that the obtuseness or ignorance of some executive officer was at the bottom of his troubles. Actually, he was the victim of the underhanded dealings of a man whom he trusted. An inspection of "The personal files of Dr. Runge" preserved in the archives of the Prussian Staatsbank (then Seehandlung) has revealed the secret. All of Runge's letters to the heads of the Seehandlung eventually came to the desk of E. E. Cochius for scrutiny and recommendation. Runge never knew this. The directors of the Seehandlung considered Cochius the person in ultimate charge at Oranienburg, and the technical director Runge played a minor role so far as the real heads of the business were concerned. The business director was the key figure because everything was measured in terms of sales and profits. It is not surprising that the wishes and plans of Runge were not always reported by Cochius as "reasonable proposals." If the latter had seconded all of Runge's suggestions, what would have become of his own position of authority? Consequently, a clear limitation had to be imposed on Runge's brilliant but revolutionary plans. The letters which passed between the two are still in the files and they give a revealing picture of business intrigue.

Cochius bought the chemical works from the financial institution on September 4, 1850. One of his early moves was to give Runge notice that his services were being terminated. Runge left on December 31, 1952, but from time to time acted as consultant. He received a pension of 400 talers per year and was allowed to keep the small house where he had lived for so many years. He also received his fuel free. The business apparently did not prosper and Cochius committed suicide in 1855. The widow and Runge soon found themselves at odds. Several years previously Runge had discovered a method of preparing artificial Chile saltpeter, which he had discussed with Cochius before the latter died. (When he tried to interest another industrialist in this "German guano," the latter responded that "it would be criminal presumptiousness to wish to imitate the excrement of a bird.") When Runge now disclosed his process to the government authorities, Mrs. Cochius was enraged because she maintained it was her property, since the research had been done in her factory. She informed Runge that he was entitled to his pension only if he supported the chemical works by words and deeds. He replied that his pension was in payment of services rendered long since, and that the house and stove wood, in value about 150 talers per year, was a small return for the advice which he gave her employees whenever they came to him for help. His invention was his own, and as a faithful servant of the state he felt it his duty to give it to the government, particularly in war time. She at once ordered him to give up the house and made difficulties about paying the pension. Since the business was steadily growing worse, it was evident that she would never pay. It was indeed fortunate that Friedrich Wilhelm IV of Prussia had granted Runge a state pension of 350 talers to be paid out of the bank funds. Runge tried to get the officers of the Seehandlung to force Mrs. Cochius to pay the original pension, but new men had come into power and nothing was done. The chemical factory was sold

[19] RUNGE, F. F., "Zur Farbenchemie. Musterbilder für Freunde des Schönen und zum Gebrauch für Zeichner, Maler, Verziehrer und Zeugdrucker. I Lieferung. Dargestellt durch chemische Wechselwirkung." In 1855 he published a continuation, "Der Bildungstrieb der Stoffe. Veranschaulicht in selbständig gewachsenen Bilder," privately printed at Oranienburg.

once more in 1857, and Runge tried to get the Seehandlung to force the new owner to respect his pension rights. Once more, nothing came of his efforts. This is truly a sad picture of mistreatment of a man who had served both his employer and the government well and faithfully for many decades.

CLOSING YEARS

Runge never married and he developed many of the typical idiosyncrasies of the lifelong bachelor. He was much interested in household problems and cleverly employed his chemical knowledge, for instance, for the removal of stains. He developed excellent recipes for such things as sour herring and cucumber salad, designed to be easily digested even by "the members of the widely ramified society of the toothless." He was an expert on canning meats and vegetables and was also very skilled in making wines from various fruits. He loved to give dinners at which he proudly displayed his culinary skill. His cleaning woman had to follow an exact routine and everything had its place in his modest home.

After he was put out of his house by Mrs. Cochius in 1856, he moved to a neighboring one belonging to his friend Lange, a stove maker. Here he spent the last ten years in the company of a few chosen companions. He kept himself busy throughout this period, puttering a little, writing much for newspapers and magazines, and composing his last large book: "Household Letters."[20]

Runge's Gravestone

The following notice appeared in the *Oranienburger Wochenblatt:*

> After a brief illness, Dr. Friedlieb Ferdinand Runge, Professor of Technology, died this morning at six o'clock in his 74th year. This notice is published with great sorrow in the name of his local friends by the undersigned.
>
> The services will be held on Thursday, March 28, at four in the afternoon, and the mourners are requested to assemble at my residence.
>
> March 25, 1867
>
> Grutzmacher, Second Bürgermeister

Although a few honors came to Runge in his later years, to most of the world he was unhonored and unsung. Two years after his death, an appeal was made to the members of the German Chemical Society for donations to place a memorial at his grave. In 1872, A. W. Hofmann, then president of the society, was able to announce that the goal had been reached. It was he who, in 1843, had shown the importance of Runge's distillation products and confirmed his findings. The obelisk was erected in 1873. The bronze medallion shows a relief of Runge's profile. This was torn away by vandals in 1923, but the German Chemical Society replaced it. The rear of the stone bears the inscription: "Dedicated to the memory of the chemical investigator by friends and colleagues." The sum of 300 marks was given for perpetual care.

The centenary of Runge's birth was fittingly remembered on February 8, 1894. The memorial address was given by Witt in the name of the Chemical Society. A memorial tablet was placed at the main entrance of the Oranienburg Palace.

Runge's last residence and death place was marked in 1923 by the "Heimatkündliche Vereinigung Oranienburgs und Umgebung." The plaque reads: "In this house lived and died Professor F. F. Runge, the discoverer of carbolic acid and aniline." The present parsonage in Billwärder was marked by a Runge memorial plaque on October 10, 1936. A section dedicated to the preservation of documents and other Runge memorabilia was set up in the Oranienburg Heimat- und Binnenschiffahrtsmuseum.

In the course of time the old Nicolai Cemetery became run down and was practically abandoned. Accordingly, by order of the municipal council, Runge's remains and the monument were moved to the new city cemetery on November 22, 1949.[21]

[20] RUNGE, F. F., "Hauswirtschaftliche Briefe," Berlin, 1866.

[21] TRANSLATOR'S NOTE: The history of the dye industry, beginning with natural indigo and madder, and stressing the sad story of Runge, has been told most interestingly by K. A. Schenzinger in his historical novel "Anilin," published in Berlin in 1936. This fictionalized account of an important chapter in chemical history has gone through many printings. It thoroughly deserves a wider circle of readers and should be translated into English.

o o o

A RAOULT'S LAW EXPERIMENT FOR THE GENERAL CHEMISTRY COURSE

Manometry Without a Manometer

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MANY simple (and basically similar) experiments on freezing-point depression and boiling-point elevation are to be found in laboratory manuals for general chemistry courses. As presented in most textbooks, however, these two colligative regularities are derived from Raoult's law as the more fundamental generalization. The authors have failed to discover in any laboratory manual an experiment illustrating Raoult's law that is adapted to the skill of the average college freshman and to the very limited supply of equipment and materials normally available to such a student. Basically, the problem posed is that of making a manometric measurement without a manometer, and without the use of a vacuum system, quantities of mercury, etc. This report offers an account of an experiment that meets this problem—an experiment requiring a laboratory time of no more than three hours, involving no difficult manipulations, and no principles that cannot be fully understood by the students.

The experiment was tested with a group of the members of a freshman course in general chemistry designed for students who have performed competently in a secondary-school course in chemistry. The experiment was well received by these students. Since the experiment was carried through during the fourth week of the course, it may be presumed that it would fall within the grasp of even beginning students at a somewhat later stage in any adequate introductory course in general chemistry. From this experiment, we find, the student gains a clearer appreciation of the concept of vapor pressure, a thorough grasp of the usefulness of Dalton's law of partial pressures, and an improved insight into the whole subject of colligative properties.

The experimental setup consists of a graduate inverted in a beaker of water. The volume and total pressure of a parcel of air confined over water in the graduate are first determined. A sample of the liquid (pure or mixed) of which the vapor pressure is to be determined is then floated up to the surface of the water inside the graduate. As a result of the equilibrium vapor pressure generated by this liquid, the volume of the confined gas is increased (since the total pressure inside the system must remain essentially constant). And then, with the aid of Dalton's law, the magnitude of the vapor pressure can be deduced from the change in the total gas volume, as explained below.

In the tested version of this experiment, measurements were made of the vapor pressure of two volatile liquids and of two determinate mixtures of these liquids. The data obtained could then be compared with the behavior predicted by Raoult's law. The two liquids chosen must: (1) differ sharply in vapor pressure; (2) form relatively ideal solutions with one another; (3) be relatively immiscible with water or with dilute brine; and (4) be less dense than water or dilute brine. In ethyl ether and benzene were found a pair of substances meeting these criteria. Other liquid pairs might, of course, be used. A typical student result obtained by the procedure described below is presented in the table. The deviation of the measured from the calculated values is, for the most part, attributed to variations in temperature during the conduct of the experiment.

Correlation of Student Data by Raoult's Law

Mixture	*—Vapor pressure, mm. Hg—* *Measured*	*Calculated*
$^2/_3$ ether-$^1/_3$ benzene	345	356
$^1/_3$ ether-$^2/_3$ benzene	210	223
Measured vapor pressure of ethyl ether:	490 mm.	
Measured vapor pressure of benzene:	90 mm.	

Two students work together on this experiment. Each student requires the following equipment:

1 500-ml. graduate
2 large (*e. g.* 800- and 1000-ml.) beakers
1 5-ml. pipet (or large medicine dropper)
2 test tubes (with cork stoppers)
1 ruler (metric divisions)
1 thermometer (1° divisions)

The class as a whole must have access to a rough balance with capacity of more than 50 grams and to a barometer (or the reading thereof).

Each pair of students will require the following materials:

200 g. crude sodium chloride
10 ml. ethyl ether (technical grade)
10 ml. benzene (technical grade)
10 ml. of mixture *A* ($^1/_3$ mole fraction ether; $^2/_3$ mole fraction benzene)
10 ml. of mixture *B* ($^2/_3$ mole fraction ether; $^1/_3$ mole fraction benzene)

The fire hazard can be reduced if the mixtures are pre-

viously prepared and issued as such (in test tubes) to the students.

In the succeeding sections there are presented: (1) a condensed version of the introduction to the experiment issued to the students; (2) a full account of the procedure; and (3) a few questions that serve to focus the students' attention on some significant points that they might otherwise fail to appreciate.

INTRODUCTION

You are to measure the vapor pressure at room temperature of ethyl ether, of benzene, and of some ether-benzene mixtures; and you are to determine the extent to which these data are correlated by Raoult's law. To begin, a sample of air is trapped over water in an inverted graduate. By measurement of the total pressure ($P°$) of the confined gas (air plus water vapor) the partial pressure of the air ($p_a°$) can be obtained. Let $V°$ represent the volume of the trapped gas, let $T°$ be the measured temperature, and let $p_w°$ be the vapor pressure of water at this temperature. By Dalton's law we may then write:

$$p_a° = P° - p_w°$$

The liquid of which the vapor pressure is to be determined is then brought in contact with the confined gas. The liquid volatilizes until a new state of equilibrium is reached with a total gas volume V^1 at a total pressure P^1 and a temperature T^1 (to which there corresponds a vapor pressure of water represented as $p_w{}^1$). Let p_a^1 represent the partial pressure of air in this mixture.

Since the total amount of air present in the confined gas has remained constant, the combined form of Boyle's and Charles' laws tells us that:

$$\frac{p_a° V°}{T°} = \frac{p_a^1 V^1}{T^1}$$

Whence, with the aid of the first equation, we find:

$$p_a^1 = \frac{T^1 V°}{T° V^1}(P° - p_w°)$$

But, from Dalton's law, we know that the final total pressure must represent the sum of the partial pressures of the individual gaseous species present. Therefore we write:

$$P^1 = p_a^1 + p_L + p_w^1$$

and from this equation solution is readily made for the only unknown, p_L, the vapor pressure of the liquid in question.

There are two practical complications to the experimental method you will use. The first is that, if there is a substantial difference in the water levels inside and outside the graduate, then the total internal pressure (P) may differ appreciably from the measured barometric pressure (P_B). However, if the level of the liquid inside the graduate is found to be h mm. higher than that outside, the following equation permits us to make due allowance for the hydrostatic head:

$$P = P_B - \frac{h}{13.6}$$

The second complication arises from the fact that ether and benzene are not completely immiscible with water. However, this miscibility is easily reduced to a negligible value by solution of sodium chloride in the water. At room temperature this salt is far too involatile to make any contribution to the total pressures inside the system.

PROCEDURE

Both benzene and ethyl ether have high vapor pressures and form dangerously explosive mixtures with air. Keep spillage of your liquid samples to an absolute minimum. No flames are to be present in your section of the laboratory at any time during this experiment.

Prepare a solution of 50 g. of sodium chloride in 725 ml. of water in a 1000-ml. beaker. When all the salt has dissolved, add hot water in small portions until the solution is within one degree of room temperature. (*Do not heat the water with your Bunsen burner.*) Fill a 500-ml. graduate with the salt solution. Place an inverted 800-ml. beaker over the top of the graduate, and rapidly invert this assembly over the sink. By cautiously raising the graduate, allow about 150 ml. of air to enter it. Then pour salt solution into the 800-ml. beaker until it is about half filled. Allow time for the system to come to room temperature. While waiting, prepare a similar apparatus into which introduce approximately 300 ml. of air.

When thermal equilibrium has been attained, record the temperature of the water, the exact volume of the trapped gas, the difference in the height of the water inside and outside the graduate, and the barometric pressure. In your textbook, find the vapor pressure of water at your working temperature. Secure a sample of ethyl ether for introduction into the graduate with 150 ml. of trapped gas, and a sample of benzene for introduction into the graduate with 300 ml. of trapped gas. A sample half filling a large test tube will be ample. Keep the tubes stoppered, and take care not to heat the liquids by handling the tubes. To introduce a sample, raise the graduate until its mouth is only slightly below the water level in the beaker. Then, with your 5-ml. pipet, carefully inject the appropriate liquid into the graduate, taking care that no air enters or escapes. The sample should be added until a separate layer can be seen floating on the water inside the graduate. Agitate the graduate until the gas volume is no longer changing rapidly, adding more sample if the floating layer disappears. During this agitation hold the graduate by its base, rather than by its barrel, so that the gas it contains will not be heated by the warmth of your hand. You are advised to conduct these operations with your apparatus in the sink, since there may be an overflow of brine from the beaker. When the gas volume in the graduate is no longer changing rapidly, set the system aside to equilibrate for at least 30 minutes—while you proceed to another portion of this experiment.[1]

When equilibrium has been reached, record the new volume of the gas, the difference in the height of water inside and outside the graduate, and the temperature of the water. If it is possible to equalize the water levels inside and outside the graduate no hydrostatic correction will be required.

After completion of the above experiments, the two setups should be cleaned, and then recharged with *fresh* brine solution. Measurements are now to be made on two ether-benzene mixtures. On the basis of your previous results, estimate the optimum initial gas volume, remembering that the greater the initial volume the greater will be the sensitivity of the measurement, but that the final volume must not exceed 500 ml. The two ether-benzene solutions have mole fractions $^1/_3$ ether-$^2/_3$ benzene, and $^2/_3$ ether-$^1/_3$ benzene. These solutions should be injected in large excess; the use of 15 or 20 ml. of each is advisable. Otherwise, proceed as before.

Calculate the vapor pressures of ether, of benzene, and of the two mixtures, by the method outlined in the introduction. Prepare a graph showing the variation of vapor pressure as a function of the mole fraction of ether. On the same graph draw the vapor-pressure curve predicted by Raoult's law. Does the system ether-benzene show significant deviations from Raoult's law?

QUESTIONS

(1) Does the presence of the layer of liquid on top of the water in the graduate significantly affect the accuracy of the pressure measurements? Under what condition(s) might this effect be significant?

(2) How would a change in temperature during the afternoon affect your results?

[1] The instructor may combine this experiment with some related exercise. In the authors' laboratory the students carry out an experiment on freezing-point depression while waiting for the establishment of equilibrium in the present experiment.

(3) The accuracy of your volume measurements is not much better than 5 ml. Suppose that, in your work with benzene, the final volume was actually 5 ml. more than you observed. By how many mm. of mercury would your determination of the vapor pressure of benzene then be in error?

(4) If, instead of charging the graduate with a large excess of ether-benzene mixture, you had added just barely enough mixture to leave one drop unvaporized, what additional source of error would then be introduced? Can this same error occur when the vapor pressure of pure ether or pure benzene is measured?

(5) The addition of salt to the water used in the experiment changes the vapor pressure of the water and changes the density of the water. Does neglect of these changes introduce significant errors into the results obtained?

A promising alternative to the experiment here described would involve the issue of ethyl ether (labeled as such) and the issue of benzene as a substance of unknown molecular weight. The student would then be instructed to prepare, from portions of these liquids, two solutions of known composition by weight. Then, on completing measurements of the vapor pressure of the two pure liquids and of the two mixtures, he would find it possible both to verify Raoult's law and to obtain an approximate molecular weight for the unknown. Were it desirable to have a series of unknowns of different molecular weights it would, no doubt, be possible to find suitable liquids other than benzene. Finally, it ought also to be possible to use as unknowns involatile solids soluble in ether but not in water.

CALORIMETER FOR DETERMINING HEAT CAPACITIES OF LIQUIDS

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THE determination of heat capacities of liquids requires knowledge of the temperature rise of a liquid caused by the addition of a known amount of heat. Heat is typically introduced as electrical energy dissipated in a heater immersed in the liquid.[2] Although the determination of energy input is easily accomplished by classical methods, the associated instrumentation is relatively complex and expensive. The minimum requirements are a storage battery, voltage divider, standard cell, potentiometer, standard resistor, galvanometer, and a timing mechanism. This paper describes a method for utilizing a constant-power heating device which obviates the need for this mass of equipment, yet permits moderate accuracy in determining heat capacities of liquids.

To utilize a constant-power source for introducing electrical energy, one need only know the magnitude of the power dissipated in a heater and multiply it by the time applied:

$$H = \frac{E^2}{R}t \qquad (1)$$

where H is the energy added to a system during time t, and E and R are the voltage drop and resistance of the heater. E^2/R is a constant in this case and we may write:

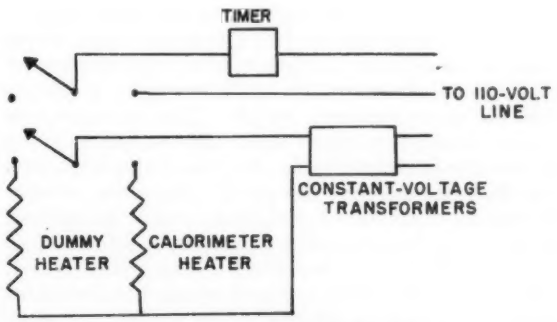

Figure 1. Calorimeter Heater-Timer Circuit

$$H = kt \qquad (2)$$

where k is a constant.

The constant k could be determined calorimetrically by using two liquids of known heat capacity. Two liquids are necessary since some of the electrical energy raises the temperature of the calorimeter whose heat capacity is generally not known. Using equation (2):

$$kt_A = C_{pA}\Delta T_A + C_{cal.}\Delta T_A \qquad (3)$$

$$kt_B = C_{pB}\Delta T_B + C_{cal.}\Delta T_B \qquad (4)$$

where t_A and t_B are the heating periods of two liquids of heat capacities C_{pA} and C_{pB}, and ΔT_A and ΔT_B are the temperature rises of these liquids in a calorimeter of heat capacity $C_{cal.}$.

To determine the heat capacity of any liquid in the same calorimeter:

[1] Present address: Aerojet-General Corporation, Azusa, California.

[2] WEISSBERGER, A., "Physical Methods of Organic Chemistry," 2nd ed., Interscience Publishers, Inc., New York, 1949, Vol. I, p. 773; VOLD, R. D., *J. Am. Chem. Soc*, 59, 1516 (1937).

TABLE 1
Calculated Temperature Rises of Water at 25°C.

ΔT (°C.)	$T_{av.}$ (°C.)	*Heating time (min.)*
1.807	25.0	10.000
1.810	25.0	10.001
1.813	24.8	10.000

$$kt_x = C_{px}\Delta T_x + C_{\text{cal.}}\Delta T_x \qquad (5)$$

where the subscript x refers to the liquid in question. Solving equations (3), (4), and (5) for C_{px}:

$$C_{px} = \left[\frac{(C_{pA} - C_{pB})}{\left(\frac{t_A}{\Delta T_A} - \frac{t_B}{\Delta T_B}\right)}\right]\left(\frac{t_x}{\Delta T_x} - \frac{t_A}{\Delta T_A}\right) + C_{pA} \qquad (6)$$

and k and $C_{\text{cal.}}$ need not be evaluated.

APPARATUS

A Sola constant-voltage transformer, 95–125-volt primary, 6.3-volt and 2.38-ampere secondary, was used as a source of constant potential. The primary was fed by another constant-voltage transformer, since line-voltage fluctuations of 20 per cent had been noted. Fourteen ohms of No. 30 B.S. manganin wire were used as a heater, and since temperature rises were approximately 2°C., the resistance of the heater was essentially constant. Figure 1 illustrates the electrical portion of the apparatus. The electrical timer, which could be estimated to 0.001 minute, and calorimeter heater were activated by one position of a double-pole double-throw toggle switch. The other position activated a dummy heater of the same resistance as the calorimeter heater so as to stabilize the transformers. Figure 2 shows the calorimeter containing stirrer, Beckmann thermometer, and heater. The calorimeter vessel was a Dewar flask equipped with a S/T 45/50 joint. The flask was closed with a rubber stopper that held the thermometer, two-hole ceramic insulator for heater leads, and a glass bushing for the stirrer. Bare heater wire was wrapped around the stem of the thermometer for one inch immediately above the mercury bulb. The heater was soldered to the heavy copper leads which were twisted around the thermometer stem. An all-glass stirrer was driven at a constant rate by an electric motor. During operation the calorimeter was wrapped with fiberglas to prevent sudden changes in room temperature from interfering with temperature drifts.

TABLE 2
Some Values of Specific Heats (cal./g.)

Source	*Benzene*	*Carbon tetrachloride*
This work	0.4125	0.2073
	0.4137	0.2065
[a]	0.4133	0.2030
[b]	0.4096	0.1972
[c]		0.2066

[a] Richards, W. T., and J. H. Wallace, *J. Am. Chem. Soc.*, **54**, 2705 (1932).
[b] Williams, J. W., and F. Daniels, *ibid.*, **46**, 1569 (1924).
[c] Vold, R. D., *J. Am. Chem. Soc.*, **59**, 1518 (1937).

EXPERIMENTAL PROCEDURE

The transformers are stabilized by passing current through the dummy heater. Approximately 250 milliliters of liquid are weighed, adjusted to the desired temperature, and added without splashing to the calorimeter. After assembly, stirring is begun. Following 10 minutes of stirring, time-temperature readings are taken every minute until a linear foredrift is established. The heater and timer are simultaneously activated by throwing the toggle switch. After a temperature rise of approximately 2°C., heater and timer are deactivated. Time-temperature readings are taken every minute until a linear afterdrift appears. A temperature rise is calculated by extrapolating fore- and afterdrifts to the midpoint of the heating period. The temperature of the heat capacity is taken as the average temperature of the fore- and afterdrifts extrapolated to the beginning and end of the heating period. Drifts were approximately ±0.003–6°C./minute, temperature being estimated to ±0.001°C. with a magnifying glass.

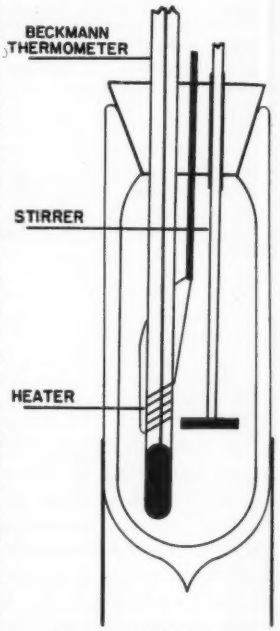

Figure 2. Calorimeter

CALIBRATION AND ACCURACY

Calibration of the calorimeter was effected by using water and *n*-heptane, which have been recommended as heat-capacity standards.[3] Table 1 illustrates the precision that was attained with this apparatus in three determinations of the temperature rise using water as the calibrating liquid.

Accuracy is shown in Table 2 by comparison of two determinations of the specific heats of both benzene and carbon tetrachloride with values found in the literature.

The excellent agreement of the specific heats is no doubt due to the fact that any systematic inaccuracies in the temperature and time would have no effect on C_{px}. From equation (6) it can be shown that a one per cent error in determining ΔT_x will affect C_{px} of benzene and carbon tetrachloride by 1.26 and 1.30 per cent, respectively.

[3] Ginnings, D. C., and G. T. Furukawa, *J. Am. Chem. Soc.*, **75**, 522–7 (1953).

THE USES OF THE ULTRACENTRIFUGE[1]

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IN MAKING an appearance of this kind there are two general thoughts that I might develop. I could attempt to treat the subject "Thirty years of colloid chemistry" or I could seek to trace my own experiences with the title "Thirty years in colloid chemistry." This is the period of time which has elapsed since I received my final university degree. Actually, in the time available I shall be able to do neither, but I do want to make a short and simple analysis of what appear to me to be the trends in colloid chemistry during this era before speaking in more detail about a subject within the general discipline with which I have become associated, namely, that of sedimentation analysis and the uses of the ultracentrifuge.

The theoretical and experimental methods for the study of colloids and macromolecules have been vastly improved and developed since the days of Graham and more recently of Einstein, and Zsigmondy and Perrin. Thus, the electron microscope has replaced the ultramicroscope as the tool for the study of particle size. With it not only colloidal particles but also the larger macromolecules are now made visible, and one can determine by direct observation the size and shape of individual virus, hemocyanin, and certain polysaccharide macromolecules. Again, size distribution curves for the classical inorganic colloids are made readily available from measurements made on the electron microphotographs.

For the organic macromolecules of the protein chemist and the high polymer chemist, the ultracentrifuge has become an important instrument for the absolute determination of molecular weight and weight distribution. Along with its development have come greatly improved procedures for the observation and description of linear and rotary diffusion phenomena.

With the passage of these 30 years the emphasis in colloid chemistry has shifted from the inorganic to the organic systems. With the new tools it has become possible to contribute to the understanding of the functions of these organocolloids in life processes and in technology. It is largely through them that our subject has become closely allied to biochemistry and medicine on the one hand, and high polymer chemistry on the other.

As we come to the consideration of my own participation perhaps I may be permitted to remark that two courses which I took at the University of Wisconsin made a deep and lasting impression upon me. One of them, given by Professor T. Svedberg in 1923, described the subject "colloid chemistry" and the other, presented by Professor P. Debye in 1927, treated the topic "polar molecules." I am sure you are familiar with the two well known monographs which form the printed record of these lectures.[2,3]

Superficially the two subjects might have seemed to be far apart; actually, it has turned out that they have many points of close relation. The title of one of my earlier articles[4] "Dipole theory and the size of molecules," is suggestive of one important point of connection, especially when I remark that were I now to assign the title I would use the word "macromolecules" instead of "molecules." At this time and with the use of the dipole theory, remarkably close estimates were made of the molecular weights of such protein molecules as ovalbumin, serum albumin, hemoglobin, and zein, the object having been stated to be "the hope the results obtained in this way may supplement those made available by using the more common sedimentation, diffusion, and osmotic pressure methods."

One interesting result of this particular endeavor was the fact that the zein, which we now know must have formed a highly polydisperse system, gave an average molecular weight of 22,000 from its time of relaxation, while the minimum molecular weight found in textbooks of biochemistry was 100,000. It was a direct result of my desire to prove what I considered to be the essential correctness of my own result that I became interested in sedimentation analysis. It did not matter that we discovered later that the higher (so-called minimum) value was based solely upon an analytical amount of an amino acid in the protein which was eventually shown to be completely absent; we were already embarked on a program of research built around the ultracentrifuge.

The subject, "The uses of the ultracentrifuge," is a broad one. In ultracentrifugal analysis there are two distinct approaches. The machine itself must be one in which convection currents due to temperature inequalities along the column and vibrations due to rotor unbalance are eliminated, so that proper mathematical analyses can be made either of the movements (sedimentation velocity) or of the redistributions (sedimentation equilibrium) of the components of a solution as the rotor revolves at a constant angular velocity. Relatively low speeds of a few thousand revolutions per

[1] Presented as the Kendall Award address at the 127th Meeting of the American Chemical Society, Cincinnati, March, 1955.

[2] SVEDBERG, "Colloid Chemistry," Chemical Catalog Co., Inc., New York, 1924.

[3] DEBYE, "Polar Molecules," Chemical Catalog Co., Inc., New York, 1929.

[4] WILLIAMS, *Trans. Faraday Soc.*, **30**, 723 (1934).

minute are sufficient to give sedimentation rates of the same order as the diffusion rates of proteins and organic high polymers, and so to produce a measurable redistribution of concentration at sedimentation equilibrium. High speeds of some 50,000 to 75,000 revolutions per minute are required to overcome diffusion and produce a moving boundary, the rate of movement of which can be said to be observed in sedimentation velocity experiments.

For this reason an ultracentrifuge laboratory should possess equipment to study solutions and suspensions at centrifugal forces from a few times gravity up to the highest attainable forces. There are several types of successful ultracentrifuge on the market, so they need not be now described. The machine itself must be provided with a suitable optical system for the process under observation. The particular choice seems now to be shifting from a system based upon ray optics (Lamm, Philpot, Svensson) to one which makes use of wave optics (Rayleigh, Gouy, Jamin), because of the greater inherent accuracy of the latter.

THEORY

The concentration distribution of small, monodisperse particles settling through a viscous medium in various force fields has been the subject of a number of theoretical investigations.[5] The attempt, limited in scope, will be made here to develop what we shall call an "equation of the ultracentrifuge," and to show that from it there may be obtained suitable equations for use with the actual data of sedimentation equilbrium and sedimentation velocity experiments.

Before going ahead we wish to observe that there are two general approaches in an effort of this kind—the kinetic and the thermodynamic analyses of the problem. The former utilizes a microscopic picture of the colloidal system and provides the simplest derivations of equations to describe the observed phenomena. The equations derived by using the kinetic analysis approach validity only very near to infinite dilution. On the other hand, thermodynamics considers the over-all energy of a mass of material rather than the molecular motions in it, and can be applied rigorously to any system at (or nearly at) equilibrium. Very important, it provides a means for extending the laws of infinite dilution to high concentrations.

It is our present opinion that not enough attention has been paid to the fact that the equations as ordinarily printed and used are limiting laws. They have usually come from a kinetic analysis, so they do not make allowances for the effects of solute-solvent and solute-solute interactions. Some of them have led to a vast literature devoted to determinations of the shape of macromolecules and what is called their extents of solvation. This is a subject upon which we shall later comment.

[5] MASON AND WEAVER, *Phys. Rev.*, **23**, 412 (1924); WEAVER, *ibid.*, **27**, 499 (1926); FAXEN, *Arkiv. Mat., Astron., Fysik*, **21B**, No. 2 (1929); LAMM, *ibid.*, **21B**, No. 2 (1929); ARCHIBALD, *Phys. Rev.*, **54**, 371 (1938); SVEDBERG AND PEDERSEN, "The Ultracentrifuge," Clarendon Press, Oxford, **1940**.

In the thermodynamic analyses there are a few basic notions which we shall use. The motion of an uncharged macromolecule in an ultracentrifuge is defined by the sum of the centrifugal potential, $\frac{-M\omega^2x^2}{2}$, and the chemical potential, μ_2, *i. e.*, the total potential, $\bar{\mu}_2$, and the frictional resistance with which the large molecule opposes the motion. If the macromolecule is charged, the potential of the electrical field must be included with the others to give the total potential. Since our equations *apply only to a two-component system* we shall use the subscripts 1 and 2, the former for the solvent and the latter for the solute. We need not have been so restricted in the treatment of the sedimentation equilibrium problem.

For sedimentation equilibrium the underlying thought is that the total Gibbs potential for the solute of the system is constant throughout the cell, *i. e.*:

$$\bar{\mu}_2 = \mu_2 - \frac{M\omega^2x^2}{2} + z_2\phi$$

In this completely general equation M_2 is the molecular weight of the solute, z_2 is its valence, ϕ is the electrical potential, ω is the constant angular velocity of the ultracentrifuge rotor, and x is the distance from the center of rotation.

For sedimentation velocity the negative gradient of total potential measures the driving force on the macromolecule. At constant velocity of fall of the macromolecule this driving force becomes equal to the frictional force, or:

$$f_2\left(\frac{dx}{dt}\right)_2 = -\left(\frac{\delta\bar{\mu}_2}{\delta x}\right)_t$$

where f_2 is a frictional coefficient.

Where a molecule is caused to sediment in a centrifugal field, neither diffusion (with gradient of chemical potential as driving force) nor the frictional resistance of the molecule to motion can be neglected. It is this thought which leads to the development of the equation of the ultracentrifuge. It contains cases of both sedimentation equilibrium and sedimentation velocity. In the latter case we are still restricted to a two-component noncompressible system. We shall consider the behavior of an uncharged macromolecule. Then the total potential of this component is:

$$\bar{\mu}_2 = \mu_2 - M_2\frac{\omega^2x^2}{2}$$

The symbol μ_2 represents the chemical potential of the constituent at the actual pressure p. At constant temperature and composition the variation of μ_2 with pressure is described by the equation:

$$\mu_2 = (\mu_2)_{p_o} + \int_{p_o}^{p}\frac{\delta\mu_2}{\delta p}\,dp$$

where $\frac{\delta\mu_2}{\delta p} = \bar{V}_2$ = partial molal volume = $M_2\bar{v}_2$, p_o = pressure at the meniscus in the cell, and $dp = \omega^2 x\,\rho\,dx$, where ρ = density of the *solution*. The quantity M_2

is the molecular weight of the solute, and $\bar{v}_2$ is its partial specific volume.
Thus:

$$\bar{\mu}_2 = (\mu_2)_{p_0} - \frac{M_2\omega^2}{2}\left(x^2 - 2\int_0^x \bar{v}_2\rho x\, dx\right)$$

On the molar basis, the driving force on the solute molecule is:

$$F_2 = -\frac{\delta\bar{\mu}_2}{\delta x} = M_2\left(\frac{d^2x}{dt^2}\right)_2 + f_2\left(\frac{dx}{dt}\right)_2$$

This is the equation of motion.

Since the acceleration $(d^2x/dt^2)_2$ is negligible, and since $(\mu_2)_{p_0} = (\mu^0_2)_{p_0} + RT\ln y_2c_2$, we write for the equation of the ultracentrifuge:

$$\left(\frac{dx}{dt}\right)_2 = -\frac{RT}{c_2f_2}\left(1 + c_2\frac{d\ln y_2}{dc_2}\right)\frac{\delta c_2}{\delta x} + \frac{M_2\omega^2x}{f_2}(1 - \bar{v}_2\rho)$$

In this equation c_2 is the concentration of solute (volume basis) and y_2 is its activity coefficient.

Sedimentation Equilibrium. At equilibrium $\left(\frac{dx}{dt}\right)_2 = 0$. For the ideal case, where $y_2 = 1$, and with a homogeneous solute,

$$M_2 = \frac{RT}{(1 - \bar{v}_2\rho)\omega^2}\frac{dc_x/dx}{x\cdot c_x} = \frac{dc_x/dx}{c_x\cdot 2Ax}$$

where $\frac{1}{2A} = \frac{RT}{(1-\bar{v}_2\rho)\omega^2}$, $\bar{v}_2$ is the partial specific volume of the solute, and c_x is its concentration at a distance x from the center of rotation.

If the system is not ideal, the molecular weight as a function of solute concentration may be expressed by the formula:

$$\frac{1}{M_2} = \left(\frac{1}{M_2}\right)_0 + Bc$$

where $(1/M_2)_0$ is the reciprocal of the true solute molecular weight, *i. e.*, at infinite dilution. In an equivalent expression:

$$(M_2)_0 = \frac{dc_x/dx}{c_x(2Ax - B(dc/dx))}$$

The constant B is used as a measure of the nonideality of the solute.

In nonideal and heterogeneous systems the expressions become still more complicated. However, the experiment does make available several of the different types of average molecular weight and thus the means to describe the heterogeneity. More complete thermodynamic theory and the application of some molecular weight-distribution functions are found in two recent publications from this laboratory.[6]

Sedimentation Velocity. The quantity $\delta c_2/\delta x = 0$ over much of the cell. The sedimentation coefficient may be a function of concentration but not of pressure.

For the ideal case with the two component system, then:

$$M_2(1 - \bar{v}_2\rho)\omega^2x = f_2(dx/dt)_2$$

with the sedimentation coefficient being defined as $s_2 = (dx/dt)_2/\omega^2x$. When the sedimentation rate $(dx/dt)_2$ has been observed, there is still an unknown quantity, the frictional coefficient f_2. It is ordinarily evaluated by an independent observation of the diffusion coefficient, since according to kinetic theory, $f_2 = RT/D_2$, at infinite dilution. The familiar Svedberg equation has been obtained by substitution to give $M_2 = \frac{RTs_2}{D_2(1-\bar{v}_2\rho)}$. We note now that the density ρ becomes that of the solvent in which the macromolecule is suspended, and $\bar{v}_2$ is the partial specific volume of the solute. The values of s_2, D_2 and $\bar{v}_2$ are extrapolated to infinite dilution of the solute after correction of s and D for the viscosity effects of the solvent. The procedure of extrapolation is an arbitrary but practical one.

The customary derivation of the Svedberg equation is based upon kinetic theory and is unsatisfactory from several points of view. An outline of the thermodynamic argument is here given, again with the caution that it applies strictly only to a two-component system, one in which any volume changes which occur as a result of the transport process are negligible. The frictional force, a frictional coefficient multiplied by a velocity, is set equal to the negative of the gradient of total potential, thus:

$$\begin{aligned} f_2\left(\frac{dx}{dt}\right)_2 &= -\left(\frac{\delta\bar{\mu}_2}{\delta x}\right)_t = -\left[\frac{\delta}{\delta x}\left(\mu_2 - M_2\frac{\omega^2x^2}{2}\right)\right]_t \\ &= -\left[\left(\frac{\delta\mu_2}{\delta x}\right)\left(\frac{\delta p}{\delta x}\right) - M_2\omega^2x\right] \\ &= -\omega^2x\,[M_2\bar{v}_2\rho - M_2] \\ s_2 &= \left(\frac{dx}{dt}\right)_2\Big/\omega^2x = \frac{M_2(1 - \bar{v}_2\rho)}{f_2} \end{aligned}$$

The usual sedimentation velocity experiments are performed in three-component systems, but their evaluation and the common computations for the size, shape, and degree of solvation of the dissolved macromolecule are based upon equations such as those given above which apply strictly only to two-component, incompressible systems.

The equations descriptive of the sedimentation velocity behavior in three-component systems are still pretty much a matter of the future, but progress in this direction has begun. Hooyman and associates[7] *claim* to have derived the Svedberg equation in the framework of the thermodynamics of irreversible processes which permits a rigorous definition of all the quantities involved, putting the nonequilibrium case on a basis which meets the same requirements of exactness as the equilibrium equation. Gosting, Baldwin, and Dunlop[8] have initated what seems to be a very significant program in the study of interacting flows in liquid diffusion.

The quantity s is described as a coefficient, not a

[6] Goldberg, *J. Phys. Chem.*, 57, 194 (1953); Wales, Adler, and van Holde, *J. Phys. Colloid Chem.*, 55, 145 (1951).

[7] Hooyman, Holtan, Mazur, and DeGroot, *Physica*, 19, 1095 (1953).

[8] Gosting, Baldwin, and Dunlop, forthcoming publications.

constant. It is somewhat variable with solute concentration. In addition, it changes with the pH and ionic strength of the solution. It is independent of the field strength, $\omega^2 x$.

In the case of a polydisperse solute one speaks of a distribution of sedimentation coefficients, $g(s)$, which specifies the weight fraction of the sample with sedimentation coefficients:

$$g(s) = \frac{1}{c_o}\frac{dc}{ds}$$

Here c_o is the total concentration and $\frac{dc}{ds}$ is the derivative of the plot of s versus concentration of material having a sedimentation coefficient less than or equal to s. When the effects of diffusion are negligible and the sedimentation coefficients are constant, independent of concentration, $g(s)$ is obtained directly from the boundary gradient curve of $\frac{\delta c}{\delta x}$ versus x, according to the equation:

$$g(s) = \frac{\delta c}{\delta x}\,\omega^2 t x^3 / c_o x^2{}_o$$

The relationship between x and s is given by the integrated form of the definition of sedimentation coefficient, *i. e.*, $x = x_o e^{s\omega^2 t}$. Thus, x_o is the distance between the meniscus and the center of rotation. In general, it is necessary to make allowance for the effects of diffusion and of variation of sedimentation coefficient with concentration in finding $g(s)$.

USES OF THE ULTRACENTRIFUGE

The use of centrifugal force in many important roles in industry is known to all. As a person representing the University of Wisconsin, it is natural that I should mention the Babcock cream separator as an example. But the instrument here involved might be termed a supercentrifuge as contrasted with the ultracentrifuge of the scientific laboratory, the machine of vibration-free and connection-free sedimentation with which we are now concerned. The quantitative measurement of sedimentation (and diffusion) behavior has provided means for the assignment of molecular characteristic constants to proteins and other polymeric materials.

The existence of well defined macromolecules in solution was proven by physical-chemical studies of protein solutions. The colloidal character of proteins was early recognized, but it was actually a matter of surprise when sedimentation analysis proved that many, if not most of the soluble proteins were built up of well defined molecular units. With the establishment of this fact there followed a rapid development of the tools themselves and of the extensions to a wide variety of the macromolecules of biology and medicine and of technology. More gradually, but none the less surely has come the realization that the sedimentation methods may be also used with success in investigations with smaller molecules. Some suggestions are made in the following paragraphs of their wide variety of applications. Since the sedimentation velocity experiment is the more familiar one it will be given preference in the discussion.

Sedimentation Velocity. The utility of the ultracentrifuge is nowhere better demonstrated than in the determination of the molecular weight for the soluble globular proteins by using the familiar Svedberg equation. That this is a whole subject in itself will be at once evident if reference is made to the Svedberg and Pedersen monograph or to more recent reviews of Lundgren and Ward[9] or of Edsall.[10] It is of course the familiar application.

There are times when one wonders if the application of this basic equation has become too familiar. We have noted that many users of the excellent machines now in use apply this equation in the evaluation of experiments with complicated systems (solvent, buffer and supporting electrolyte, protein). In addition, there has been built up a voluminous literature devoted to the assignment of shapes and extents of hydration to protein molecules. These molecular characteristics come from operations with the frictional force in the velocity problem. Obviously the sedimentation coefficient is a function of both of them, but at present there is no way to separate the effects of each in the modification of the frictional coefficient. The kinds of trouble into which one can get are well stated in the introductory paragraphs of a recent article in which the hydrodynamic properties of proteins are considered.[11] In a few words, the true hydrodynamically effective volume of the protein molecule in solution is inaccessible to exact definition. To this extent, at least, these authors have performed a valuable service even though to test the validity of their alternate approach seems at the moment to be quite out of the question. Sedimentation and diffusion coefficients are not known to within anything like the accuracy which would be required for the equations.

The familiar equations of Herzog, Illig, and Kudar and of Perrin have been put to use to compute the molecular characteristic dimensions of many highly elongated and even flexible macromolecules, but an examination of the assumptions underlying the development of these equations should have caused restraint. The type of difficulty into which one can be led is well illustrated by the literature pertinent to the shape of gelatin molecules in saline solution. It had been assumed, as before in the case of the globular proteins, that one dealt here with molecules whose form could be approximated as ellipsoids of revolution, so dimensions were assigned and much was said and even written about the mechanism by which plasma extender gelatin was lost after infusion into human veins, and how these molecules could be modified chemically to give them longer retention times per given molecular size. Actually, the gelatin molecules in solution take

[9] LUNDGREN AND WARD, in GREENBERG, Editor, "Amino-acids and Proteins," Thomas, Springfield, 1951.

[10] EDSALL, in NEURATH AND BAILEY, Editors, "The Proteins," Vol. I, Part A. Academic Press, Inc., New York, 1953.

[11] SCHERAGA AND MANDELKERN, *J. Am. Chem. Soc.*, 75, 179 (1953).

the form of randomly-kinked chains;[12] thus the mechanism of elimination from the body is entirely different from that which had been envisioned. In this way there is explained the fact that gelatins, whether or not they have been subjected to chemical treatments, show little if any differences in retention times provided the simple average molecular weights are alike.

Now we are getting away from the purpose of the report. What I am trying to express is my belief that more attention should be devoted to the development and extension of the basic theory of the sedimentation velocity method, to put it to use in the determination of quantities which can be made the subject of exact definition. Molecular weight is one of them. It now can be said that even though the protein cannot be obtained in what the physical chemist would call pure form, the work of Drs. Gosting and Baldwin has made it possible to obtain the molecular weight of a homogeneous protein which is present as a major constituent of the system under observation. The experiments must be performed in dilute solution to eliminate or at least minimize the effects of any flow interaction of diffusion.

In polydisperse systems the distributions of sedimentation coefficient have been or are being evaluated for protein systems such as casein, gelatin, the gamma globulins, and the beta lipoproteins; and for polysaccharide systems such as the dextrans, glycogens, starches, and the pneumococcus polysaccharides. There are difficulties inherent in all of them. For example, in the case of the beta lipoproteins there is superimposed a distribution of sedimentation coefficients which is based upon solute density differences upon that which goes with variations in size and shape. One might proceed by making separations of the lipoproteins into classes of like densities prior to the analytical sedimentation velocity experiments, to give sedimentation coefficient distributions of size and shape in each density class. This appears not to have been done in the experiments of Gofman and associates and one wonders about the interpretation of their experiments.

The usual methods for the determination of sedimentation coefficients are based upon observations of a "moving boundary." It is also possible to obtain such data by using experiments in which accumulations of solute are determined. Thus, in the case of smaller molecules, often of great biological interest, the procedure is to determine the flow of solute through an arbitrary plane in the region of uniform concentration in the ultracentrifuge cell. This approach has been successfully utilized in the assignment of sedimentation coefficients to a number of polysaccharides of low molecular weight, and even to glucose. These are again two-component systems, and an adequate theory is available.

Biochemists are now beginning to use an experiment based upon the idea of accumulation, to provide sedimentation coefficient data for a protein constituent of some characteristic activity which has not been separated from other constituents. The system is now a multicomponent system, so that very carefully controlled experimental conditions are now required to insure a reasonable result.

The sedimentation-velocity method is beginning to be applied in the study of organic high-polymer systems, but many problems of theoretical and practical kinds remain to be worked out before the results can have fundamental and quantitative significance. At the pressures known to exist in the ultracentrifuge cells, the organic solvents become more dense and more viscous but the pressure dependence of these quantities is not accurately described in the literature and proper corrections cannot be made of observed sedimentation rates for reduction to standard conditions.

The low centrifugal force machine has the advantage that it is effective, not only in connection with sedimentation-equilibrium studies of the kind now to be listed, but also for operation as a sedimentation-velocity instrument to describe the particle size distributions in finely divided materials which extend from the finest of inorganic colloids up to particles large enough to measure by means of an ordinary good microscope. As examples, mention may be made of paint pigments, carbon-black suspensions, emulsions of neoprene latex, colloidal gold, etc. The particle size distribution is often an important variable in determining the ultility and merit of the powdered material. For instance, the covering power and tensile strength of a paint depends upon this distribution.

Sedimentation Equilibrium. Substantial progress has been made in the detailed study of the molecular weight, state of aggregation in solution, and molecular-weight distribution of a number of organic, long-chain high polymers, particularly cellulose, cellulose derivatives, rubber, rubber substitutes, polysaccharides, lignins, etc. In some cases there has been established the relationship between viscosity and molecular weight, in others the correlation between sedimentation constant and molecular weight, the purpose being to give valuable information about molecular form in solution. The unique description of the molecular mass heterogeneity has been worked out in principle, but in practice, using the optical systems based upon ray optics, the result is ordinarily subject to some arbitrariness. At the present time the equilibrium experiment is more satisfactory than the velocity one for observations of the heterogeneity in the systems containing flexible, long-chain molecules.

The sedimentation equilibrium method also offers new possibilities for the study of the inorganic electrolytes and polyelectrolytes. In the case of the former the experiment provides data for the determination of the activity coefficients of the solute, since at equilibrium the total potential (the sum of the chemical, electrical, and centrifugal potentials) does not vary with distance in the cell.

For the polyelectrolytes (sometimes called "colloidal electrolytes") new possibilities are provided for the study of micelle formation or solute association in

[12] Williams, Saunders, and Cicirelli, *J. Am. Chem. Soc.*, 58, 774 (1954).

detergent and dye systems. In the case of the detergents an unfavorable density difference between solute and solvent (water) makes the experiments difficult. Certainly studies will eventually be made of the condition of the solute in solutions of the alkali silicates, stannates, tungstates and molybdates as it depends upon solute concentration and the presence of other electrolytes.

Combination of Sedimentation Velocity and Sedimentation Equilibrium. During recent years much has been learned about the means by which corrections for the effects of nonideality of solution can be made in both sedimentation-velocity and sedimentation-equilibrium experiments. The importance of these corrections cannot be overemphasized. With them, the results of sedimentation-equilibrium and sedimentation-velocity experiments can be combined to give two kinds of new information. For polydisperse systems in the equilibrium case, mention has been made of the fact it is practically necessary to assume a general form of the distribution function.[6] This means that any minor details of the distribution will fail to make their appearance. This is not true with the velocity diagrams and their evaluation, because any arbitrary distribution of sedimentation velocities can be handled. In the combination of the two experiments the latter distribution can be converted to a distribution of molecular weights to obviate the difficulty. Furthermore, there can be evaluated the relationship between sedimentation coefficient and molecular weight, $s = kM^{a}$, at infinite dilution, to provide information about shape of the macromolecules in solution.[13]

[13] WILLIAMS, *J. Polymer Sci.*, **12**, 351 (1954); WILLIAMS AND SAUNDERS, *J. Phys. Chem.*, **58**, 854 (1954).

By this combination there may be achieved a sedimentation analysis, which was Svedberg's original purpose. It has been a long time in development, the chief reason being that there have been difficult problems in taking apparent values of sedimentation coefficient and molecular weight and converting them to data which are valid at infinite dilution.

ACKNOWLEDGMENT

For advice and help in connection with the development of a research program in sedimentation analysis I am greatly indebted to many teachers, associates, and graduate students. Their number is large, so that mention by name is not practical; nonetheless, the distinction of the 1955 Kendall Company award is conferred upon them as well as upon me.

I do wish to record here the fact that it was Dr. Warren Weaver of the Rockefeller Foundation and President E. B. Fred of the University of Wisconsin who saw to it that an earlier small effort of mine was enriched by the purchase, installation, and maintenance of two ultracentrifuges, nearly 20 years ago.

Over the years the scientific program has received substantial financial aid from the University of Wisconsin, the Wisconsin Alumni Research Foundation, the Rockefeller Foundation, the National Institutes of Health, the Office of Naval Research, and other institutions. I am greatly indebted to them.

To two of my most recent associates, Drs. L. J. Gosting and R. L. Baldwin, I must make an especial acknowledgment. High loyalty and devotion on the one hand, and unusual scientific ability on the other, are combined to an extraordinary degree in them.

MORE MNEMONICS

For Naming the Aldohexoses:

"All altruists gladly make gum in gallon tanks," serves to recall *d*-allose (0*L*), *d*-altrose (2*L*), *d*-glucose (3*L*), *d*-mannose (2*L*, 3*L*), *d*-gulose (4*L*), *d*-idose (2*L*, 4*L*), *d*-galactose (3*L*, 4*L*), *d*-talose (2*L*, 3*L*, 4*L*). The *L* refers to the position of OH group on the left; all other OH groups are on the right. The number refers to the carbon position starting with the aldehyde group.

For Naming the Dicarboxylic Acids:

"Oh my such good apple pie serve a slice" reminds one of the first letters of oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azaleic, and sebacic acids.

For Naming the Amino Acids Essential to the Diet of Rats:

"Any help in learning these little molecules proves truly valuable," gives the first letters of arginine, histidine, isoleucine, leucine, threonine, lysine, methionine, phenylalanine, tryptophan, and valine. For the human, drop "any help" and the corresponding amino acids, arginine and histidine.

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[EDITOR'S NOTE: Professor Will S. DeLoach of Catawba College, Salisbury, North Carolina, is making a collection of mnemonics found useful by chemistry teachers. Reference to previously published items and original contributions are requested.]

THE INTRASEMESTER ONE-HOUR EXAMINATION

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THE giving of one-hour examinations during the semester (quarter or term) is a general practice in American colleges and universities. Very probably others have had some qualms about the effectiveness of these examinations. It is hoped that the opinions expressed here may stimulate others to make a more critical appraisal of them.

The first question to be considered is: "What are the essential functions or purposes of examinations given during the semester?" The answers commonly given, either explicitly or implicitly, may be summarized briefly by the two statements:

(1) To provide the instructor a basis for assigning the student a grade in the course.

(2) To encourage (or impel) the student to review the subject matter covered and to show how well he has *remembered* the facts and/or principles involved (and, according to many students, also the personal opinions expressed by the instructor regarding certain matters).

Certainly grades on these examinations do provide, in part, the basis for determining the final standing of the student in a course, but most would agree that this should be an incidental, although necessary, function. There is considerable doubt whether grades on the one-hour examinations are satisfactory criteria (even in part) for determining the student's final standing—or perhaps better, the student's mastery of the subject matter of the course.

The second answer is the one most commonly given. It should be noted that the word "remember" is italicized. Memory is, no doubt, an essential factor involved in effective learning. However, it seems justifiable to assume that, *per se*, it is excessively stressed (and weighted) in most one-hour examinations. One need only ask what fraction of the questions given in these examinations can be answered correctly from memory alone. That substantially all the questions should be of this type is a necessary consequence of the very limited time available for the examination.

What, then, can be done about examinations given during the semester? Before discussing this question, the following answer to the question regarding the essential functions or purposes of intrasemester examinations is proposed:

To enable the student to develop the ability to think critically and effectively about the questions or problems involving the subject matter of the course, and, of equal importance, to express his ideas (answers) in a clear and concise manner.

Surely one-hour examinations cannot be expected to accomplish these purposes. How then? It is proposed that intrasemester examinations be "open-book" and be written outside the classroom. The only restriction on the student should be that he shall not discuss the questions with others. He should be permitted to use any source material, such as texts, reference books, etc., available to him. This will require that the questions (or problems) on the examination shall be such that they will require correlation, integration, and evaluation of the facts and principles covered in a way that cannot be found explicitly in any source material. Granted that the preparation of such examinations will require the application of considerable time and thought by the instructor. This fact may provide the subconscious motivation for some of the objections to this type of examination.

The time allotted the student to complete such an examination will vary. If a course has three class meetings per week, such an examination may be issued at the close of one class period and returned at the beginning of the following period, with no class meeting intervening. Or the examination may be given out at the close of a class hour preceding a vacation period of reasonable length, and returned at the first of the class hour following the vacation. The latter procedure has been practiced by the author during the past year with classes of students in physical chemistry. The consensus of the students has been that these examinations have enabled them to understand and appreciate the subject matter much more effectively and satisfactorily. Without exception the students—irrespective of their relative ability—who honestly and objectively desire a thorough understanding are enthusiastically in favor of such examinations. What better criterion is there of the effectiveness of our methods?

Such examinations as these may not be feasible in lower division (freshman and sophomore) courses. Reasons for believing that they more surely and effectively fulfill the essential functions of intrasemester examinations than do one-hour examinations seem convincing. That such examinations should generally prevail in graduate courses will probably not be gainsaid.

A MICRO AIR-FLOW REACTION APPARATUS

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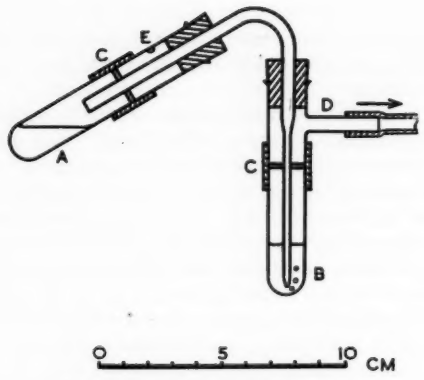

Figure 1. Micro Air-flow Apparatus

THE manipulation of volatile materials or reagents is often facilitated by operating in the gaseous phase, the vapor being diluted with and carried along by a stream of noninterfering "carrier" gas. For obvious reasons, air is used as the "carrier" whenever such choice is practicable.

The micro air-flow apparatus shown in Figure 1 is a development of the forms previously described (*6*, *7*). Evolution vessel *A* and reception vessel *B* are 50- × 12-mm. crystallizing tubes (made by cutting down half-inch test tubes) and are easily attached to or detached from rubber-tubing sleeves *CC*. When gentle suction is applied to the side arm of T-piece *D*, the stream of air drawn in through the small hole in glass-tubing sleeve *E* carries volatile material from *A* into *B*. A typical example of the use of the apparatus is in the detection of ethanol, etc., in microsaponification distillates (*5*). The volatile carbonyl compound produced by dichromate oxidation is carried over into *B* and is there precipitated as the 2,4-dinitrophenylhydrazone.

Passage of air through the liquid in *B* should not be too rapid; about two bubbles per second is a suitable rate. Since the required degree of suction is very slight, an aspirator provides a steadier flow than does a filter pump. When, as in the example above, the run is complete in less than five minutes, an ordinary 50-ml. buret filled with water makes an admirable aspirator (*7*).

When the material in the evolution vessel has a tendency to foam or froth, *A* may be replaced by a longer vessel, *e. g.*, a 4- × $^1/_2$-in. rimless test tube. An example is in the formation of acrolein by the dehydration of glycerol (*1*).

At the bottom of a long evolution vessel, place one small drop of glycerol and add about one gram of powdered potassium hydrogen sulfate. In the reception vessel, place two ml. of saturated 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid. Assemble the apparatus, apply gentle suction, and heat the evolution vessel to melt the reaction mixture. To control the considerable frothing, apply the flame toward the upper part of the mixture. Orange acrolein-2,4-dinitrophenylhydrazone should rapidly precipitate in the reception vessel; when the melt ceases to froth, dismantle the apparatus, filter off the precipitate, wash with water, suck dry, and recrystallize from ethanol.

The handling of toxic volatile reagents, *e. g.*, nitrogen dioxide, hydrogen cyanide, phosgene, etc., may also be carried out with this apparatus, slight modifications being made as required. The reagents may either be generated from suitable mixtures placed in the evolution vessel or released from previously charged melting-point capillaries. The latter will withstand an internal pressure of 70 atmospheres or more (*2*). Capillaries containing phosgene are available commercially.[1]

If capillary storage is adopted, glass sleeve *E* (Figure 1) above the evolution vessel is replaced by a T-piece similar to *D*, as shown in Figure 2. A small plug *F* of glass wool is lightly packed into the side arm, which is closed by an ignition tube *G* attached by a rubber-

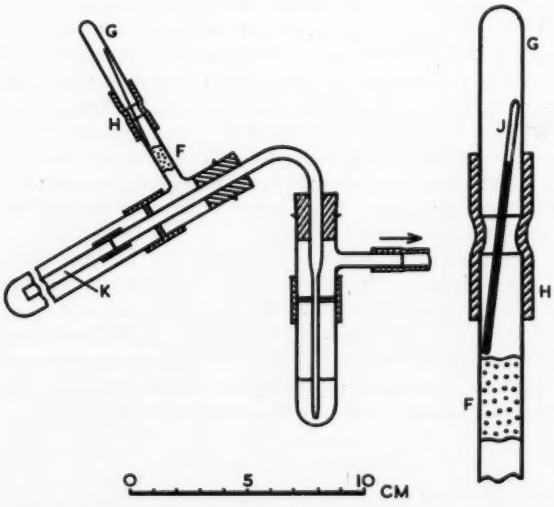

Figure 2. Modification for Capillaries Containing Volatile Reagents, and (Right) Enlarged View of Hinge

[1] J. W. Towers & Co. Ltd., Widnes, Lancs., England.

tubing "hinge" *H*. This arrangement, shown on a larger scale at the right, enables capillary *J*, containing the volatile reagent, to be broken when required by pressing *G* sideways. The evolution vessel is left empty and, to "buffer" the rush of vapor when the capillary is broken, should be from 4 in. to 6 in. long. Suction is not applied until the capillary has been broken, and about half a minute later *G* should be detached so that an air stream may carry over the remaining vapor. If the latter is dense it may tend to form a pocket at the bottom of the evolution vessel; in such cases, extension *K*, attached to the transfer tube and reaching toward the bottom of the evolution vessel, is useful.

An example of this technique is the carbonation of *p*-chlorophenol by means of phosgene (*1*). Twenty milligrams of the solid are dissolved in two ml. of 2 *N* sodium hydroxide and the precipitated di-*p*-chlorophenyl carbonate, obtained after allowing air flow to continue for about 10 minutes, is recrystallized from methanol.

Replacement of sleeve *E* by a second T-piece is also useful when entry of moisture into the system must be avoided, since a desiccant tube containing fused calcium chloride, etc., may be attached to the side arm of this T-piece.

The version of the air-flow apparatus shown in Figure 3 is, with the exception of delivery tube *L*, assembled from standard "Quickfit" interchangeable semimicro components.[2] The delivery tube is the standard air-leak tube MF 15/OS with a female joint attached to the bead. This modified tube is also useful for its original purpose, *viz.*, in reduced-pressure distillation, since a fine-control stopcock (*3*) carrying a male joint may be attached when required (*8*).

Alternative devices for breaking the capillary are also shown in Figure 3. If the device shown at (*a*) is adopted, the position of the glass-wool plug should be adjusted until the tip of the capillary enters the way of the stopcock plug. Slight rotation of the latter then causes the capillary to fracture. After any initial pressure surge has died out, the plug is either eased in the barrel or pulled right out, thus allowing aspiration to be proceeded with.

The fracturing device shown at (*b*) and (*c*) likewise permits materials other than glass to be kept from contact with the reagent. The male half of the ball joint is formed merely by fusing the end of the tubing in a blowpipe flame, passing a stream of air through the bore to prevent the latter from becoming constricted. The upper end is then closed by fusion as shown. A tool made from copper sheet is used to form the female half and, after forming, the half-joints are ground into one another with fine carborundum paste. This is conveniently done by holding the male half in the chuck of a slow-speed electric drill or stirrer and applying the other half with a rocking motion to produce a spherical seating. After removal of abrasive and

[2] Rochester Scientific Co., 38 Scio Street, Rochester 1, N. Y.

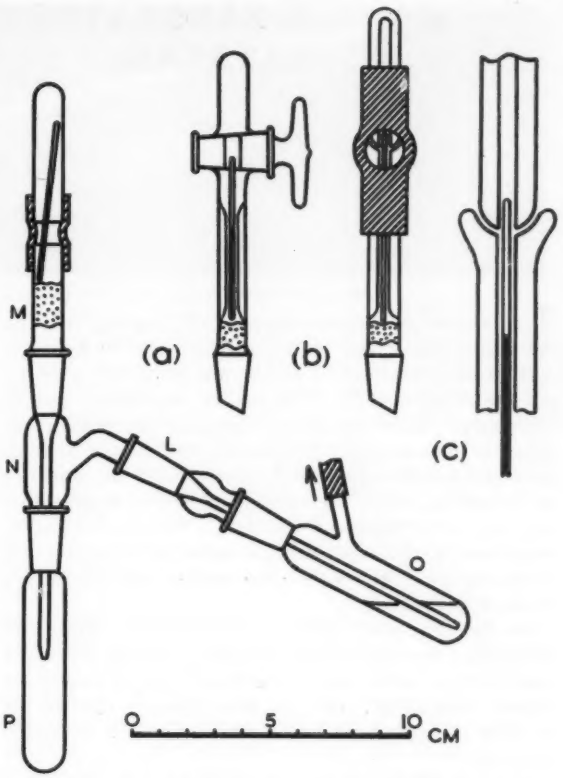

Figure 3. Air-flow Apparatus Assembled from "Quickfit" Parts

L, Catalogue No. MF 15/OS with added female joint; *M*, No. MF 15/-OS; *N*, No. SH 4/000; *O*, No. MO 60; *P*, No. MF 24/0/4; (*a*), (*b*), and (*c*), alternative devices for fracturing capillary.

examination, the halves may be lapped together with polishers' rouge. A short length of soft rubber tubing which firmly grips the walls of the half-joints constitutes the tensioning device (*4*). A pair of diametrically-opposed holes are cut with a sharp cork borer, thus relieving inward pressure around the joint and allowing ample flexibility for the breaking of a capillary without causing the joint to open. When it is desired to commence aspiration, the joint is lightly pulled apart and the male portion is thrust through one of the holes in the tensioning device. Air may then freely enter the female portion.

LITERATURE CITED

(1) Lidstone, A. G., Cyclostyle notes, Ministry of Education Course for Teachers of Chemistry in Technical Colleges, London, 1948.
(2) Rees, T., *Anal. Chem.*, **26**, 226 (1954).
(3) Stock, J. T., and M. A. Fill, *Analyst*, **71**, 142 (1946).
(4) Stock, J. T., and M. A. Fill, *Metallurgia*, **36**, 54 (1947).
(5) Stock, J. T., and M. A. Fill, *School Sci. Rev.*, **33**, 331 (1952).
(6) Stock, J. T., and M. A. Fill, J. Chem. Educ., **30**, 296 (1953).
(7) Stock, J. T., and M. A. Fill, *ibid.*, **31**, 144 (1954).
(8) Test Report No. 4, *Laboratory Practice*, **4**, 50 (1955).

A LABORATORY DEMONSTRATION OF BLOOD CATALASE

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THE recent calorimetric method of Landahl[1] for the determination of the blood catalase level is a simple and rapid procedure, suitable not only for research purposes[2] but also for a laboratory experiment in biochemistry. The method is especially interesting because it demonstrates graphically, by means of temperature rise, the remarkable effect which the presence of a small amount of enzyme can have in accelerating the rate of a chemical reaction. We have found it expedient to demonstrate the experiment to the biochemistry students when they begin their laboratory work on enzymes.

In the Landahl method a measured amount of hydrogen peroxide solution is added to a buffer solution containing a small amount of blood, the solutions are mixed thoroughly, and the temperature rise of the mixture is noted. The decomposition of hydrogen peroxide:

$$H_2O_2 \rightarrow H_2O + {}^1/_2O_2$$

is an exothermal reaction. In the presence of a catalyst, especially in the presence of catalase, the decomposition reaction proceeds at a rate sufficient to liberate heat more rapidly than it can be lost from the system to the environment; hence the resultant temperature rise. Since the degree of acceleration of the reaction is, within certain limits, proportional to the catalase activity, it is possible to estimate that activity from the amount of heat liberated. To simplify the method Landahl measured not the heat liberated, but the maximum temperature rise of the solution under standardized conditions. The standardization of conditions include: (*a*) pH, nature, and amount of buffer, (*b*) amount of H_2O_2, (*c*) amount of blood, (*d*) nature of thermal insulation, (*e*) heat capacity of the final solution, container, and thermometer.

[1] LANDAHL, H. D., *Proc. Soc. Exp. Biol. Med.*, **84**, 74–9 (1953).
[2] ENGLANDER, H. R., I. L. SHKLAIR, R. Q. BLACKWELL, AND L. S. FOSDICK, *J. Periodont.*, **26**, 233 (1955).

THE METHOD

The original article by Landahl[1] should be consulted for the discussion of the various modifications which he studied. The procedure to be described below, a slight modification from Landahl, proved to be most satisfactory for our purposes. (The equipment, part of which appears in Figures 1 and 2, and solutions mentioned in the procedure will be described briefly after the procedure.)

Preparations to Be Made Prior to Drawing Blood Sample.

(1) Add exactly 4.50 ml. of pH 7.0 buffer solution to each of a number of plastic tubes, stopper, and place in a thermostatted water bath at 25°C.

(2) Place a suitable sample of 30 per cent H_2O_2 in the 25°C. water bath.

(3) Shake down the mercury in the clinical thermometers and place them along with an Anschütz thermometer in the 25°C. water bath.

(4) Check the temperature of the wooden block and bring it to 25°C. by use of large, water-filled test tubes (previously equilibrated to 25°C. in the bath) immersed in the holes with the cork collars removed.

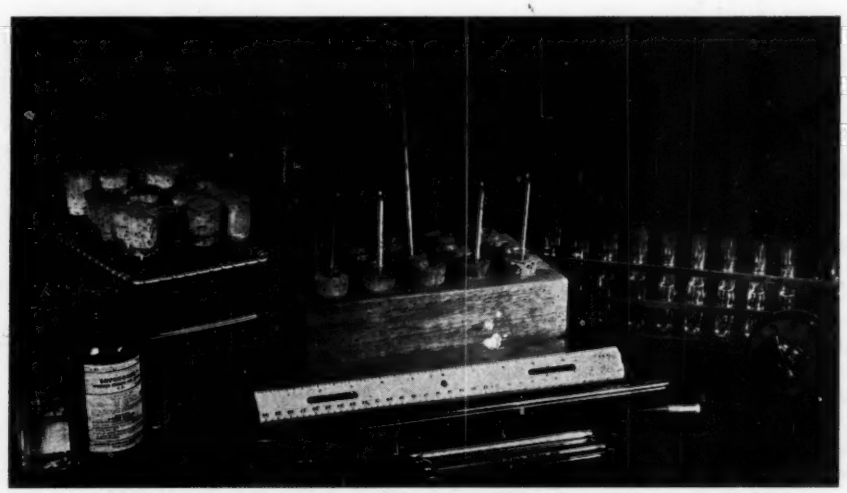

Figure 1. Equipment Used for Catalase Determination

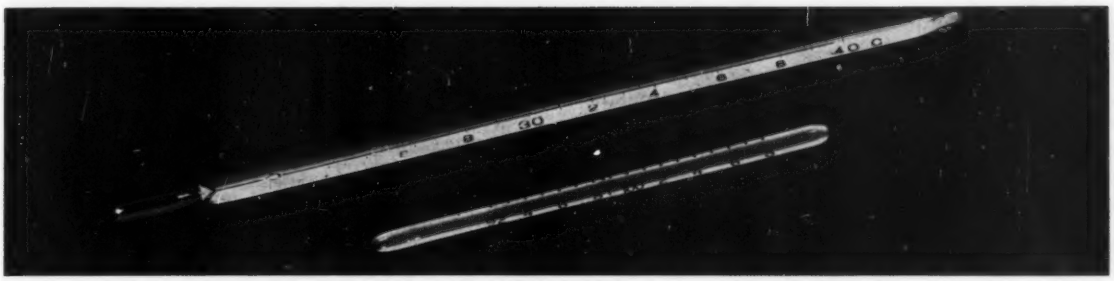

Figure 2. Comparison of Regular Clinical Thermometer with Special Type Used in This Work

Remove the tubes and replace the cork collars when the experiment is ready to begin.

Experimental Procedure.

(1) Prick the finger or ear lobe of the patient and obtain exactly 0.01 ml. of blood in each of two 10-microliter pipets for duplicate determinations (use the rubber tube and mouthpiece as used with regular blood pipets).

(2) Immerse the tip of the pipet in the buffer solution, draw some solution into the pipet, expel the contents by blowing, wash the pipet by repeated drawing and expulsion of solution. (This must be done immediately to prevent the clotting of blood in the capillary of the pipet.) Repeat the operation with the second pipet in a second tube of buffer.

(3) Insert the tubes containing the 4.50 ml. of buffer plus the 0.01 ml. of blood into the wooden block support.

(4) Insert the Anschütz thermometer into each tube, stir well, and record each temperature to the nearest 0.1°C. This temperature should be in the range 25 ± 0.5°C., and preferably at 25°C.

(5) Add one small drop of capryl alcohol to each tube (to prevent loss of solution by foaming when the oxygen evolution begins).

(6) With a pipet add exactly 0.5 ml. of 30 per cent H_2O_2 to each tube, immediately insert a clinical thermometer, and stir steadily for 15 seconds.

(7) Allow the tubes to stand 10 minutes or more and record the maximum temperature reading.

(8) Subtract the initial temperature reading (obtained with the Anschütz thermometer) from the final one read from the clinical thermometer to obtain the temperature rise.

MATERIALS AND SOLUTIONS

The plastic tubes used were Lusteroid-brand celluloid centrifuge tubes, 13 × 95 mm., weight approximately 2.5 grams (Figure 1).

The wooden block was made of hardwood, $5^1/_4 \times 8\text{-}^5/_8 \times 3^1/_2$ in. It has fifteen one-in. holes, $3^1/_4$ in. deep, spaces $1^1/_2$ in. between centers. Collars for the holes were made from No. 14 corks by cutting off the tops to leave $^7/_8$ in. of height, and boring holes to provide a loose fit for the plastic tubes. The collars were inserted to a depth of about $^3/_8$ in. into the holes in the wooden block.

Pyrex tubes, 25 × 150 mm., filled with water and corked, were used to bring the wooden-block temperature to 25°C. (The tubes were always carefully dried on the outside after removal from the water bath and before insertion into the block.)

Initial temperature readings in the tubes were taken with the Anschütz thermometer, range −5 to 60°C., calibrated in 0.2°C. For the temperature rise it is much more convenient to use a maximum-temperature thermometer, such as a clinical thermometer, than to observe steadily an ordinary thermometer until the maximum temperature is reached. Landahl used ordinary clinical thermometers; however, they are usually made with a range of 92–108°F. (equivalent to 33.3–42.2°C.) so that in the experiment a temperature rise of at least 8°C. is required to register a reading. In anticipation of an occasional reading lower than this in the human and in blood other than human, we ordered special thermometers of the clinical type with a range of 25–40°C. calibrated in 0.1°C.[3] Figure 2 allows a comparison of the ordinary clinical thermometer (the smaller thermometer in the picture) with the special type. A small laboratory centrifuge is used routinely for "shaking down" the mercury thread in the clinical thermometers.

Ordinary 10-lambda micropipets were suitable for accurate measurement of the blood samples, but the blood must not be allowed to stand in the pipets.

The pH 7.0 phosphate buffer used was that recommended by Landahl (one part 0.1 *M* Na_2HPO_4 to one part 0.04 *M* NaH_2PO_4). Instead of using one ml. of this solution in each tube and adding 3.5 ml. of water[1] it is more convenient to dilute the buffer with water in those proportions (*e. g.* 1 liter buffer with 3.5 liters water) and add 4.5 ml. of the diluted buffer to each tube. (For routine determinations it is convenient to fill 100 tubes at a time, stopper, and keep refrigerated until used.) The 30 per cent hydrogen peroxide solution (Superoxol) used was used as obtained.

RESULTS

Landahl found that with 58 normal individuals the mean temperature rise produced by the action of 0.01 ml. of human blood was about 12°C. Our results on normal subjects were as follows:

[3] The special clinical-type thermometers were obtained from Rascher and Betzold, Inc., Chicago, Illinois.

Number of subjects	163
Mean temperature rise	10.9°C.
Standard deviation	1.8°C.
Range	7.2–15.2°C.

The slightly lower mean temperature rise found in our work, if not due to sampling differences, may reflect in part a difference between the standardized procedures used (one notable difference in our procedure was the use of the larger clinical thermometers which have a higher specific heat). It serves to illustrate the necessity for each laboratory to establish its own calibration curve where temperature rise is plotted versus catalase activity (in suitable units such as Keil units or Q_{cat}, etc.). For this purpose one may use standardized catalase solutions or dry samples of catalase.[4]

[4] Both standardized catalase solutions and catalase in powder form are available from Armour and Company, Chicago, Illinois.

A VARIABLE PERIODIC SYSTEM

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STUDENTS often have difficulty seeing the connection between the two usual forms of the periodic system, the one in short and the other in long periods.

The system I am about to describe is variable. It consists of separate little cards, one for each element, which are hung up on a board. This enables the system to be used in the two forms interchangeably.

The cards are colored as follows: H, dark blue; first group (Li), light blue; second group (Be), white; third group (B), green; fourth group (C), black; fifth group (N), brick red; sixth group (O), yellow; seventh group (F), light red; eighth group (inert gases), gray.

This system has two characteristics. First, the

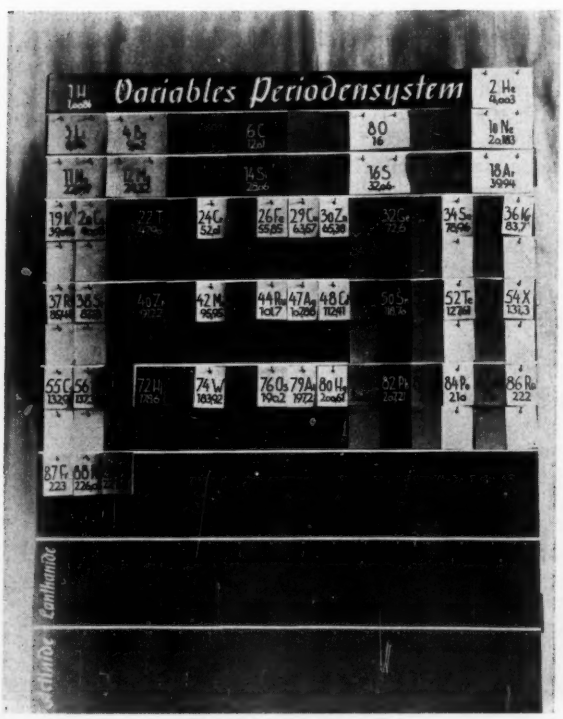

Figure 1. Long Form

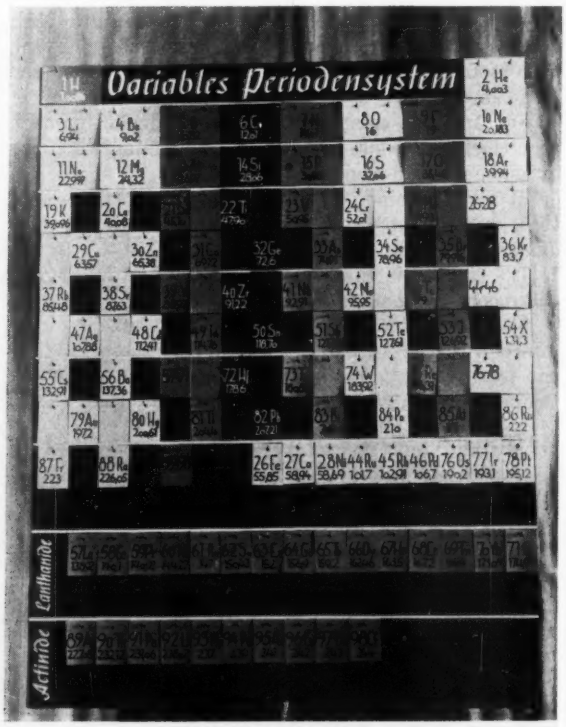

Figure 2. Short Form

cards of the lanthanides as well as those of the actinides (Ac, Th, Pa, U, and the transuranides) all hang on the same nail. In the same manner the iron metals (Fe, Co, Ni), light platinum metals (Ru, Rh, Pd), and heavy platinum metals (Os, Ir, Pt) form one block each, on separate nails. Second, there is a column after the fourth, fifth, and sixth periods which is vacant while the system is used in the long-period form; herein the system differs from the colored system in long periods by A. von Antropoff. In order to call special attention to the principal groups, the spaces between the elements are covered with blank cards.

It is easy to change from the long- to the short-period form. Figure 3 shows the fourth period; large numbers are elements of principal groups and small ones of the subgroups. First, the second half of the period is lowered one row. Then the upper half is spaced out to the right and the lower half to the left.

It now will be seen that the elements of the first and second principal groups are to be found in the upper left-hand corners and those of the other principal groups in the lower right-hand corners of their respective fields, which is characteristic of every short-period system. Now vacant spaces are filled with blank cards as mentioned, to facilitate identification of principal groups.

Blocks of cards can be substituted in the system itself by one card with special lettering, like 26–28 or 57–71. These blocks can be separated and hung on nails specially installed below the actual system.

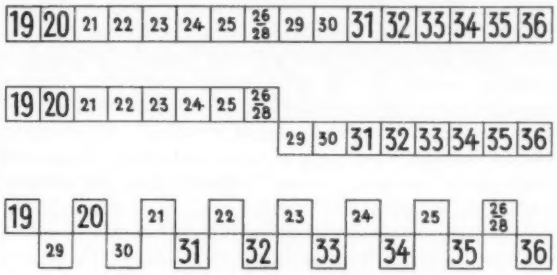

Figure 3. Transforming the Fourth Period

TIME-SAVING READING IN CHEMISTRY

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READING plays a vital role in the training and life work of a chemical engineer. For the practicing engineer reading is a never-ending must. One editor-scientist reported that about half a million scientific papers are published each year. Who reads these papers and how can the ideas be spread?

There are many problems involved in knowing what is going on in science and how to use this information. For the student, reading is the one indispensable art which may determine his college career, affect his course of study, fix the hours to be spent in daily assignments, and perhaps even keep him from majoring in science. This paper will deal mainly with the educational and improvement possibilities of reading.

Chemists and professors of chemistry are now showing more interest in such facets of reading as comprehension, speed, variability, and reading habits. Many want to know what is wrong with their reading. One reason for poor reading habits may be traced to the profession one follows. The proofreader and the chemist may be cited as examples. A reader of proof looks for misspelled words in his work. He does not read for meaning and in time he will read everything as though he were spelling silently. Proofreaders generally are slow readers, victims of their calling. They are one-way readers.

In somewhat the same way a chemist, owing to his sense of engineering accuracy, tends to be limited and hampered in general reading skills. His style is usually slow and studious as he strives for total mastery of the topic. Soon this may become his only reading skill. Chemists generally are inflexible readers. They, like the proofreader, tend to become one-way readers.

Reading is not a simple activity. It is a complex process which calls for continuing thought reconstruction during the act of reading, by the reader, based upon his background. These thoughts in turn may spark some latent ideas which may serve immediate or future needs in many ways; the needs for reading and the values attached to them may not be the same.

Reading should be purposeful and evaluative. How it should be done should depend in some measure upon why one would want to read in the first place.

Once that is recognized, purpose and interest should certainly determine the particular skill to be used in reading. Variability in reading skills is desirable and essential for most readers. Reading for the main idea, general information, reporting, pleasure, or for study should each be handled differently by the reader. These are the skills which chemists and students of engineering need to develop.

If one is reading for general information the rate of reading should be several hundred words a minute faster than when reading for study. A fast rate of, say, 400–500 words per minute should be used in reading practically all professional journals. Important articles may be handled at a somewhat slower rate, preferably on the second reading. Time yourself in reading your copy of THIS JOURNAL. It should take about two and one-half hours to read the articles and book reviews.

It is an appreciation of these different ways of reading that is needed in the training of chemists and chemistry teachers. Unwittingly, teachers through the upper grades and in colleges have kept students from becoming better readers. Lack of proper teacher direction in developing reading skills is partly to blame. Only too entrenched is the idea that a good grade is synonymous with good reading. It may be a sign of comprehension, but it is not necessarily indicative of effective reading. Frequently students are enjoined to study well when what they really need is to learn to read more efficiently. Study after reading would serve some purposes much better than study while reading.

Another stumbling block to the more facile reading of scientific articles is the hand-me-down idea that science is tough. Again our schools and society "set" a prejudice against chemistry long before the student begins to read, study, or know what chemistry is. Chemistry has always been represented to the prospective student as a difficult course. Along with that "set" goes another, namely, that technical material is hard to read. This attitude no doubt has conditioned the chemist against doing technical reading in an easier manner.

These notions need to be displaced, if for no other reason than that language itself is an abstraction. For what is chemistry to those who are capable of abstraction? It is a sign language, an abstraction, which fortunately also has many objects of art to which labels can be attached. In education we need to understand and make use of the fact that chemistry is no more difficult than the language it requires to express it. We also need to recognize that a large proportion of the population is capable of abstraction and can therefore learn chemistry. If this were done perhaps more capable students would be attracted to engineering and chemistry instead of being frightened away.

The second notion, that technical reading is difficult reading, also needs to be corrected. A question will help clear the issue. Technical to whom? A lay reader picking up a chemical magazine would find the "technical" going rough. However, there is no "technical" language to the chemist who picks up the same magazine. Technical reading for the chemist is, or should be, common reading; it is technical only to the untrained in chemistry. Here again a wrong notion may have caused many professional people to believe they could not read more efficiently. The consequences may be grave, at least reading-wise and subscription-wise; slow readers will not spend enough time reading, nor will they subscribe to the magazines pertinent to their professional growth.

The development of reading skills is important to chemists and teachers of chemistry if they expect to keep abreast of literature in chemistry and allied fields. Professors can aid students to read more effectively by helping them to understand that, *without sacrifice of comprehension*, they can improve their speed in reading by following these few simple rules.

(1) Read without looking back. If you have this weakness start now to do less of it. Some regression is permissible at times.

(2) Read to get the general idea. This is a useful skill to develop as it will really give one the chance to read rapidly. Short stories and articles of 1000–1500 words make good practice materials.

(3) Practice making fewer stops per line. For this purpose newspaper-size lines are ideal. One will not be lost for lack of interesting or challenging reading material because a number of magazines also use the narrow-width line. Do avoid fine print and closely spaced reading matter. As proficiency is acquired, one will think more in larger phrase units rather than in chopped-up, smaller, word-for-word segments.

People who read better will take the time to survey the current periodicals in the field and will also have time for careful study of the articles of greater importance. Let better reading play a vital daily role in your chemical future.

Report of the

NEW ENGLAND ASSOCIATION OF CHEMISTRY TEACHERS

THE HISTORICAL APPROACH TO CHEMICAL CONCEPTS[1]

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Sir George Williams College, Montreal, Canada

TEACHING chemistry should be easy today. Practically all the important and fundamental concepts of the science have been explained in terms of a few subatomic particles. The big four of chemistry—the electron, proton, neutron, and quantum—determine atomic and molecular structure, the periodic classification of the elements, and chemical change. Even outside of chemistry they have achieved fame in their own right, as vital components of the atomic age. Youngsters have heard about electronics, atomic energy, gamma radiation, and Geiger counters even before coming to chemistry. Surely it should not be difficult to teach the subject to such a precocious generation.

The above seems to be the philosophy of many textbooks published today. Why bother with an old and fallacious atomic theory, an incomplete and amateurish periodic table, an inadequate and superficial ionization theory, a confusing labyrinth of laws of chemical combination with roundabout methods of finding atomic and molecular weights? Instead, we could supply our students with a late model of atomic structure, furnished with electrons at carefully calculated energy levels, with power-loaded cores of protons and neutrons, all perfectly arranged in a simple scheme of atomic numbers, in a foolproof periodic chart. At the slightest flick of a mental switch, the electrons form covalent bonds or electrovalent ions. Without any effort at all we explain compound formation, isotopes, radioactivity, atomic energy, ionization, oxidation-reduction, resonance, and everything else.

In textbooks written from this point of view, Chapter One is usually an introduction to chemistry in which there is even an exposition of the scientific method, although no attempt will be made elsewhere in the book to apply the method, and Chapter Two begins the detailed description of the subatomic particles as the first step in the synthesis of the atoms and of chemistry. To illustrate, I take a few examples from a book published recently. The concept of the atom is introduced by writing:

> To the eye, matter appears as a continuous mass. However, experimental evidence kept accumulating that matter consists of discrete units. That is, one could take a portion of an element like copper and divide it into smaller and smaller particles, when a particle of such size would be reached which could no longer be divided and still retain the identity of the element. The name "atom" has been assigned to represent this smallest portion of the element.

and one imagines, surely, that the author eventually will present the experimental evidence which he implies and that the evidence will be the laws of chemical combination which gave rise to the atomic theory. About 100 pages later, within which the electronic details were elaborated, the author writes:

> The atoms of a given element will always combine in the same ratio with the atoms of another element. For example, 1 atom of carbon will combine with 2 of oxygen to form 1 molecule of carbon dioxide. Further the atoms of a given element, excluding the possibility of variation due to the existence of isotopes, all possess the same mass. *From this one can deduce the law of definite composition*—A given compound always contains the same elements in the same proportions by weight.

Examine the logic and the pedagogical philosophy. The concept of the atom is drawn from some nebulous speculation. It is then elaborated with electrons, protons, and neutrons, but all without one real shred of evidence. Finally, the law of definite composition is deduced from the electron theory of atomic structure. By placing advanced and abstract theory before experimental and verifiable fact, this presentation has completely eliminated the scientific method and thereby has deprived the student of one of the greatest dividends which accrues from a course in chemistry. In addition, it has also deprived the student of a rational understanding of the science itself.

[1] Presented before the Seventeenth Summer Conference of the NEACT, Tufts University, Medford, Massachusetts, August 17, 1955.

The law of conservation of mass, the statement and verification of which constitute an early introduction to quantitative chemistry and to the concept of the scientific law, fares no better. The author writes:

> The fact that matter and energy are interconvertible is nothing new. In 1905 Einstein enunciated the theory of equivalence between mass and energy, showing that a very simple mathematical relationship exists between them . . . One of the most fundamental laws relating to matter and energy is that expressed in the law of conservation of mass and energy; neither mass nor energy can be created or destroyed.

Again, examine the logic. First, Einstein enunciates the theory of equivalence of mass and energy. From this, we deduce the law of conservation of mass and energy. How? Why? Presumably it is nothing new —we are born with the information!

Early in the book atomic and molecular weights are introduced by stating—not deriving or justifying—what the *absolute* weights of the atoms are. For example, the student is given the information that the atom of helium weighs 6.65×10^{-24} grams, as if there were a balance on which the atom was weighed. The author then states that the commonly used atomic weights of the elements are in the same ratio as their absolute weights. From this he "derives" a number which, we are told, is called Avogadro's number. Avogadro's hypothesis must yet wait for 113 pages more to be introduced. Once again, note the inverted order —the Avogadro number before the Avogadro hypothesis, the absolute atomic weight before the relative atomic and molecular weights.

But does this method really simplify the teaching of chemistry? Or does chemistry remain a strange mixture of the real and the abstract, of the old and the new; and is it not a subject which must be taught, not only to that small minority of students preparing to become professional chemists, but also to that large number of students, both in science and liberal arts, who want to understand the subject and the scientific method for application to their own chosen fields or for the impact of these upon industry, society, and the intellectual disciplines, including philosophy? Chemistry is as real as our physical environment or the many synthetic materials which it produces; but it is as abstract as the molecules, atoms, ions, electrons, and other particles whose behavior it seeks to understand. How often have students asked, "Won't we ever be able to see electrons?" How disappointed they are when told that because of the very nature of the electron itself, it will never be visible and that all our knowledge concerning electrons is the result of experimental measurement of their hypothetical effects. How much easier teaching would be if we could exhibit mounted specimens of molecules and atoms, as the biologists shows his specimens of preserved tadpoles. We would let students stare by the hour at electronic orbits, double bonds, asymmetric molecules, or watch graceful dynamic equilibria and tautomerisms, and perhaps catch a glimpse of an electronic transition or a higher order collision between reactant molecules.

This method tries to provide a verbal microscope to make this possible. One might call it an "ultra electron microscope." Like the real electron microscope which reveals the world of colloidal dimensions, this one is supposed to reveal the world of electronic dimensions. But is it science? Or is it an evasion of our task as teachers to teach? Is it a substitution of the condescending and arbitrary "I am telling you" for the more difficult and more humble "I will prove to you so that you will understand and be able to do likewise?"

It may be conceded at once that there is no ideal method or order of teaching chemistry which can be legislated into universal acceptance; and that probably it is best that each instructor be allowed to evolve his own individual method through trial and error. If, in such a process, the establishment of a principle could be of help, it would be that wherever possible the instructor should place before the student the conditions which warranted the abstract concepts of chemistry, rather than ask the student to accept them purely on faith. In such a presentation, chronological accuracy is desirable but not essential. This approach is a synthesis of the history and the evolution of chemistry. Not only does it reveal the operation of the scientific method, but it also gives to the science a unity which is both organically vital and intellectually aesthetic. Thus, it is a prerequisite for the future chemist and a science-appreciation course for the liberal-arts student. Above all, it is not intended to be a rigorous course in the formal history of chemistry Kieffer[2] eloquently states the case for the historical approach in these words:

> Give careful attention to the order of presentation. It does not have to conform strictly to history. But do not deny to the student, when it is within his mental power to understand and to make judgment, that evidence and information by means of which he can make or understand the analyses and reach the conclusions of earlier investigators. It may be that certain things will be magnified and others diminished in stature but essentially the train of thought should be presented intact.

A few examples of such a presentation follow.

Broadly speaking, scientific chemistry had its beginnings in three developments:[3]

> (1) The discovery of the weight relationships between reacting substances, which are summed up in the laws of chemical combination and which led to Dalton's atomic theory;
>
> (2) The gas laws and the molecular hypothesis, which helped focus attention on the problem of distinguishing between atom and molecule;
>
> (3) The discovery of Galvanic current electricity, which led to the discoveries of electrolysis and of new elements; also to the first rational theory of chemical forces namely, the dualistic theory of Berzelius.

Upon this background one could project the atomic theory of Dalton as an attempt to formulate a quantitative atomic theory in contrast to the qualitative atomic philosophy which was in vogue even in the times of Boyle and Newton. The shortcomings of the theory

[2] KIEFFER, WILLIAM F., J. CHEM. EDUC., 28, 300 (1951).

[3] MOORE, F. J., "History of Chemistry," McGraw-Hill Book Co., Inc., New York, 1931.

were not, as is often stated today, that it did not describe the subatomic particles, but that Dalton, recognizing that he lacked a criterion for distinguishing between atomic and combining weights, adopted one which was arbitrary and erroneous, namely, that the most common compound of two elements was that whose molecules contained one atom of each. Dalton came to this conclusion because of his thorough acceptance of a simple molecular philosophy of gases, which led him to a collision theory of chemical reaction and compound formation.

The correct solution to the problem of atomic, molecular, and combining weights was given by Avogadro. His hypothesis, based upon the recently enunciated law of combining volumes, not only provided the method for finding molecular weights, but also distinguished correctly between the "physical" molecule and the "chemical" atom. As the acceptance of the Avogadro hypothesis grew, the concepts of the true molecular formula, valence, and chemical equations evolved. The consistent atomic weights and valences of the elements became the basis of the periodic table, while valence and molecular weights became the basis of the structural theory of organic chemistry. For the first time it became possible to classify the elements and the organic compounds in an absolute, rather than an empirical manner.

This, very sketchily, is the development of early chemical theory. The instructor may edit it—eliminating here, elaborating there. But unless some effort is made to incorporate its logical perspective into the presentation of chemical theory, the final picture is almost certain to be unintelligible to the student.

CHEMICAL CONTROVERSIES

Since this paper is on "The historical approach to chemical concepts," it might be in order to elaborate on a few of the early controversies in chemistry.[3]

The electric cell, born of the famous observation by Volta and Galvani in 1798, that strips of copper and zinc immersed in a solution of acid give rise to the electric current, soon led to the discovery of electrolysis of water, in 1805. Gay-Lussac was quick to recognize that the volume of hydrogen evolved was double that of the oxygen and his curiosity drove him to inquire whether such an integral ratio between volumes of gases involved in a chemical reaction was accidental or common. The result of this investigation was the law of combining volumes, enunciated in 1808, the same year that Dalton's atomic theory appeared in his "New System of Chemical Philosophy." Avogadro sensed that there must be a simple connecting link between the reacting volumes of Gay-Lussac and the reacting atoms of Dalton. The simplest explanation would have been to postulate that equal volumes contain equal numbers of atoms. This was inadmissible, however, as in certain reactions the volume of product was twice as great as the volume of reacting gas, and this would necessitate the splitting of the Daltonian atom in a chemical reaction. Avogadro rejected this, retaining the Daltonian concept of the indivisible atom, but postulated instead that equal volumes of gases contained equal numbers of molecules at similar conditions, thus asserting correctly for the first time that "the chemical atom and the physical molecule are not the same," a crucial point which both the atomic theory of Dalton and the molecular theory of Bernouilli could not attain. Avogadro's deductive reasoning in deriving this hypothesis stands second to none in the entire history and breadth of natural science for its brilliance and importance.

Thus, in the year 1811 chemistry possessed within its grasp an instrument of logic and insight which could give it a quantitative basis for its atomic theory, an accurate system of reckoning weight relationships, and a precise vocabulary to begin to describe what goes on in the invisible realm of molecules and atoms in the course of chemical change. Unfortunately, the hypothesis was rejected by the outstanding authorities of the time. Of course, they believed they had good reason for doing so. Electrochemistry, which had set off the sequence of events which led to the hypothesis, also provided the theory for rejecting it. By 1820 Berzelius, one of the most precise experimental chemists of all time, had thought out and proposed an electrical theory of chemical reaction according to which the atoms possessed both positive and negative electricity (we believe that today), but in unequal amounts. Hence, argued Berzelius, atoms tend to combine chemically with their electrically opposite kind to form molecules of diminished electrical strain. By the same token, atoms should reject others of their own kind, as presumably they do in such volatile gases as oxygen, hydrogen, chlorine, and nitrogen. In view of this, the diatomic nature of these gases is most improbable, and the Avogadro hypothesis which leads to such a conclusion cannot be taken seriously.

Dalton rejected the hypothesis for a reason of his own, namely, it led to such ridiculously complex formulas as H_2O for water, NH_3 for ammonia, and CH_4 for methane! Dalton believed that nature was basically simple, that chemical reaction resulted from collisions between atoms, and that therefore the most probable formula for an abundant compound was the uniatomic type like HO, NH, and CH for the above. Avogadro did not have a chance against these giants. When students find the Avogadro hypothesis "hard to take," let us remember that so too did Berzelius and Dalton.

The vindication of Avogadro came through the rise of organic chemistry. Ever important, ever mysterious, ever vast, the art of organic chemistry goes back to the witchcraft of the primitive medicine men who concocted the first potions—and no doubt the art still persists today. But the science of organic chemistry has a recorded birth-year, 1828, when Wöhler synthesized urea. This falls within the era of the Berzelius theory of electrical dualism. In 1831 Dumas, chemist of Paris,

was called upon as consultant by an angered hotel keeper and his supplier of wax candles because an important hotel ball had to be called off when the candles became to fume with "muriated gas." Upon investigation, Dumas found that a workman at the candle factory was using chlorine near the vat containing the molten candle wax and apparently the hydrocarbon of the candle combined with some chlorine. After his clients had settled their case, Dumas undertook a study of this reaction, known today as the halogen-alkane substitution reaction, for a number of important reasons. In the new compound which had been formed—the alkyl halide—chlorine, an electronegative element, had replaced hydrogen, an electropositive element. This was an apparent contradiction of the Berzelius concept of compound formation. Furthermore, it was eventually found that no less than four halogenated compounds of different boiling points could be obtained from methane alone. This suggested that methane could not have a simpler formula than CH_4, in contradiction to Dalton's formula of CH.

During the controversy which ensued between Dumas and Berzelius, the former showed that many halogen substitutions were possible and thus discovered the halogenated organic acids. Dumas also became interested in Avogadro's method for finding molecular weights and extended the method to organic liquids by contributing a technique which still bears his name. In the following decade, Hofmann investigated the chemistry of the amines, showed that at least three alkylated ammonias exist, which today we call primary, secondary and tertiary amines, and concluded that the formula for ammonia could not be simpler than NH_3. This corresponded to Avogadro's molecular weight and formula but contradicted Dalton's simple formula of NH.

About this time, too, the "minority" party of Dumas introduced the concept of organic types for classifying organic compounds. This was the forerunner of the modern homologous series. According to this concept, substitution of one group for another was possible within the "type," without reference to the electrical nature of the substituting group. Finally, in 1850 Williamson synthesized ether from alcohol and ethyl iodide and concluded that alcohol and ether were progressive alkylation of water; hence the formula for water could not be simpler than H_2O. Chemists conceded that the evidence for Avogadro's formulas was complete.

Cannizarro collected all of these ideas and published them in a pamphlet which he distributed at a convention called to iron out these difficulties. Lothar Myer, who published a periodic law independently of Mendeleev, wrote:[3]

> I read the pamphlet repeatedly and was astonished at the clearness with which the little book illuminated the most important points of the controversy. The scales seemed to fall from my eyes. Doubts disappeared and a feeling of certainty replaced them. The waves of the controversy seemed to subside and the old atomic weights of Berzelius, the combining weights of Richter and Faraday, all seemed to come into their own. As soon as the discrepancies between the Avogadro rule and the law of Dulong and Petit had been removed, both were seen to be capable of universal application. Thus the foundation was laid for determining the valence of the elements, without which the theory of atomic linking could certainly never have developed.

As the number of known chemical compounds grew and as their formulas became known with greater accuracy, the similarity between the formulas began to appear. This was first noticed by Frankland, who wrote in 1852:[3]

> When the formulas of compounds are considered, even a superficial observer is struck with the general symmetry of their constitution: the compounds of nitrogen, phosphorus, antimony, and arsenic exhibit the tendency to form compounds containing 3 or 5 equivalents of other elements, and it is in these proportions that their affinities are best satisfied. Without offering any hypothesis concerning this symmetrical grouping of atoms, it is sufficiently obvious from the examples given that such a tendency or law prevails, and that, no matter what the character of the uniting atoms may be, the combining power of the attracting elements is always satisfied by the same number of these atoms.

This passage, written in 1852, is often regarded as the first statement of valence theory. Here too, organic chemistry proved very helpful. In 1858 Kekulé came to the conclusion that when several carbon atoms occur together in a molecule they may be connected with each other. This idea, which now seems axiomatic, was highly original, and once grasped it gave the key to the molecular structure of organic compounds. The first structural formulas were written by Couper who, unfortunately, used erroneous atomic weights for oxygen. By 1861 Kekulé's text appeared, on which the foundations of modern organic chemistry are laid.

The full impact of the electron upon chemistry is also lost in the authoritarian presentation of that subject. The historical approach, on the other hand, again provides a welcome logical coherence, as well as an excellent demonstration of what Conant refers to as the "strategy and tactics" of science.[4] At the beginning of this century, pre-electron chemistry was a mass of unfinished business. There was no rational interpretation of electrochemistry and ionization. The periodic table, in spite of its power, was incomplete, empirical, and arbitrary. Structural organic chemistry and electrical inorganic chemistry had diverged so far apart that they hardly seemed to be divisions of the same science. Fundamentally, there was no theory of atomic structure or of chemical affinity. As Remick writes,[5] "The stage was set for the entrance of the conquering hero, the electron. No dramatist could have chosen a more perfect moment for ushering in the chief actor."

As far back as 1834, long before any definite concept of the ultimate nature of matter or electricity existed, Faraday discovered that there was a direct relationship

[4] CONANT, JAMES B., "On Understanding Science," Yale University Press, New Haven, 1947.

[5] REMICK, A. EDWARD, "An Electronic Interpretation of Organic Chemistry," 2nd ed., John Wiley & Sons, Inc., New York, 1949.

between the amount of electricity which passed through an electrolytic cell and the mass of matter electrolyzed in the process. The most significant point in Faraday's laws of electrolysis was that the amount of matter electrolyzed did not depend upon the temperature of the reaction, the voltage of the cell, the concentration of the solution, or other such factors which determine the extent of almost all other reactions. There were but two determining factors—the quantity of electricity and the equivalent weight of the element electrolyzed. It was not until later that the full implication of these laws was recognized. In the year 1881 Helmholtz[6] declared:

> The most startling result of Faraday's Laws is this: if we accept that matter is made up of atoms, we cannot avoid concluding that electricity also is divided into definite elementary portions which behave like atoms of electricity.

It was Stoney who first used the word electron in a similar connection. About this time he wrote:[6]

> Nature presents us with a single quantity of electricity which is independent of the particular body acted upon. To make this clear, I shall express Faraday's Laws in the following terms. For each chemical bond which is ruptured within an electrolyte during electrolysis a certain quantity of electricity traverses the electrolyte, which is the same in all substances. This definite quantity of electricity I shall call the electron.

Helmholtz and Stoney thought of electricity and electrons as an external force acting upon the atoms, not as an integral part of the atom, capable of migrating from atom to atom in the course of chemical change, as we understand the process today. That state of maturity of our knowledge was achieved through the great revolution of modern physics which began about this time and was interrupted by the outbreak of war in 1914.

The "advanced physics" involved in teaching the discovery of the electron presents no problem in this atomic age. The cathode-ray tube is as familiar as the television screen. The student also knows about X-rays and radioactivity, and welcomes the knowledge that they were discovered in logical sequence. Even Rutherford's scattering experiment is easy to describe when the student has seen full-page advertisements of department-store Geiger counters. All this provides an excellent background for the more difficult detail of Mosely's determination of atomic numbers and Millikan's determination of the charge on the electron. The instructor who wishes to impart a sense of masterful execution of a work of art in science can refer his class to Millikan's description of the preparation of his apparatus for the oil-drop experiment:[7]

> The charge on the electron is increasingly coming to be regarded not only as the most fundamental of physical or chemical constants, but also the one of most supreme importance for the solution of numerical problems of modern physics. It seemed worthwhile, therefore, to drive to the limit of its possible precision, the method herewith developed. Accordingly, in 1914 I built a new condenser having surfaces which were polished optically and made flat to *within two wave-lengths of sodium light* . . . the dimensions of the condenser no longer introduced an uncertainty of more than one part in 10,000. The voltage was determined after each reading in terms of a Weston standard cell, and are uncertain by no more than one part in 3,000. The times were obtained from an exceptionally fine printing chronograph, controlled by a standard astronomical clock which prints directly the time to hundredths of a second. All the other elements of the problem were looked to with a care which was the outgrowth of five years of experience with measurements of this kind.

Students are more likely to be receptive to the reality of the Avogadro number when they learn the true manner and precision of its determination.

Chemistry was quick to use the new ideas of atomic structure. Even before the Rutherford theory of the nuclear atom, a number of electron theories of valence and chemical reaction had been suggested. The modern theories of valence, however, are based on the Rutherford model and its subsequent refinement by the quantum theory and by wave mechanics. Lewis and others worked out the concepts of electrovalence and covalence, both normal and coordinate. Electrovalence is the modern rationalization of Berzelius' dualism, but covalence is a completely modern contribution to the theory of valence. Its absence in earlier decades was the condition which bred the controversy between Berzelius and Dumas, and the divergence between organic and inorganic chemistry.

With new theories of valence came new theories of chemical reaction. Lewis[8] defined oxidation-reduction phenomena as electron-transferring reactions, with the reductant as electron donor and oxidant as electron acceptor. In 1923 Brönsted defined acid-base phenomena as proton-transferring reactions, with the acid as proton donor and the base as proton acceptor. One of the last great research projects which Lewis carried out was to accumulate data from 1923 to 1938 to show that acid-base phenomena could also be rationalized in terms of electrons rather than protons. Lewis defined the acid as the acceptor of a pair of electrons in the formas tion of a coordinate covalent bond, while the base acts as donor of such a pair of electrons. This concept unifiechemical reaction theory by emphasizing that electronic behavior is not an intrinisic property of a substance like its color or density, but depends upon the electronic nature of the reactants with which it is coupled. Thus, water is oxidant to sodium, reductant to fluorine, acid to ammonia, and base to hydrogen chloride. Furthermore, the Lewis concept of acids and bases is of vital importance in the growing electron theory of organic chemistry.

Perhaps the most arbitrary treatment of all is given the neutron. It is often presented as merely the arithmetical difference between the atomic number and the atomic weight of an element. Yet it too has a most unusual and instructive history, not without its element of speculation, prediction, chance, error, and courage.

[6] MILLIKAN, ROBERT A., "Electrons," University of Chicago Press, Chicago, 1947, p. 12.

[7] *Ibid.*, p 117.

[8] LEWIS, G. N., "Valence and Structure of Atoms and Molecules," Chemical Catalog Co., New York, 1923.

Rutherford believed that such a particle existed and speculated about its properties:[9]

> It should be able to move freely through matter. Its presence would be difficult to detect by the spectroscope and it may be impossible to contain it in a closed vessel. It is like an invisible man passing through Piccadilly Circus; his path can be traced only by the people he has pushed aside. On the other hand, it should enter readily the structure of atoms.

When finally a highly penetrating radiation was reported as a result of the bombardment of beryllium with alpha rays from polonium, Chadwick upheld the view that this radiation was a stream of neutrons rather than gamma radiation because of the high energy of the radiation—great enough to cause the ejection of protons from atomic nuclei—and the absence of ionization along its path. Again a controversy ensued, and it was finally resolved with careful measurement and scientific objectivity. The new theory not only provided the concept of the neutron which was so useful in explaining isotopic differences, but it also provided a source of neutrons—a mixture of Be and Po—for experimental purposes, and within a few short years artificial radioactivity, artificial transmutation, and the atomic age were ushered in.

[9] RUTHERFORD, E., *Proc. Roy. Soc.* (*London*), **1920A**, 370.

CONCLUSION

These are but a few of the many issues and case-histories encountered in chemistry, whose presentation can constitute an important part of an education which is both scientific and liberal. By showing the circumstances under which problems were recognized, data accumulated, laws formulated, and theories proposed in that sequence, we are contributing to the maturing process of the students. Their power of scientific analysis, understanding, and accomplishment will grow as they are made contemporaries and witnesses of the greatest master demonstrations of the past and present. This can be achieved only with some knowledge of the history, philosophy, and adventure of science.

To the Editor:

I read the editorial of March, 1955, with considerable interest and enthusiasm, but I must also say that some feeling of doubt was left in my mind after reading and thinking of the many problems involved.

As you so aptly stated in the latter part of the editorial, "It may well be that if we are losing ground it is because we are not getting ourselves to the right places at the right time."

How serious is the situation? How urgently do we need more scientists? Are we trying to create a greater supply than demand? If a problem really exists, have we reached the point where the various scientific groups are ready to step in and assist in working out a solution to the problem?

Most readers of the scientific news are familiar with the statistics which suggest a sharp contrast between the extent of scientific training in the U.S.S.R. and the U. S. A. Furthermore, data on numbers of persons entering (and leaving!) secondary-school science teaching are frightening.

It is becoming more apparent each year that greater effort must be made to draw good science teachers to the secondary level if we are to inspire more young people to take up the science professions. Even though the problem of salary might be solved so as to offer competitive appeal with industry and universities, the problem still remains with regard to securing desirable teachers.

The American Chemical Society may claim to have set up certain standards for rating and approving those colleges and universities qualified to offer majors in the various branches of chemistry and related fields. Do they realize, however, that students attending such colleges are not inclined to enter the secondary fields of science teaching? Any graduate of these colleges who may finally go into high-school teaching will be considered to be a failure in the eyes of the great majority of his instructors and his fellow students.

Where, then, are the high-school teachers to be found? The answer is that the great number of them will come from the state colleges of education, and from those other colleges which have not been considered by the A. C. S. as worthy of accreditation by this organization.

This means that the high schools will be receiving a group of graduates who have been trained in the field of general education with little emphasis on any major field. They will have been indoctrinated in all the many generalities associated with general education, and will be completely unprepared to teach any special-

ized field. How can such a teacher be expected to inspire young people when he himself has no understanding of his subject?

Is it any wonder that many teachers in colleges and universities are beginning to express the opinion that they would rather have the student enter college chemistry with no previous training from high school? At least in this way there are no false concepts to undo before starting on the regular work of teaching fundamental principles.

With each passing year the schools of education and the "educationists" are making more and more demands for greater generalization at the expense of good sound study in one or more concentrated fields of endeavor. Some liberalized study is highly important, but where does this reach a maximum? The trend is toward more of this generalization and unless some organized effort is made to control it we will see the "educationist" continue to dictate the policies for training and certifying all teachers.

The time has come for more than talk. The situation demands a sincere and objective study on the part of many groups including the A. C. S. Unless immediate action is taken to improve the training, prestige, and salaries, to make demands relative to teacher training policy, and to lend encouragement to potential candidates, the situation can only grow worse.

If we, as interested people in the field of chemistry, allow this to go unchallenged, then it must be because we are not willing to face the situation and to be at the right place at the right time.

As one who has spent a good many years in teaching in high school, junior college, and college, I would wish we could rise to the occasion and see this problem solved. It will take the combined efforts of industry, the technical societies, and all those dedicated to the pursuit of the great principles of science.

THOMAS C. VAN OSDALL

SANTA ANA COLLEGE
SANTA ANA, CALIFORNIA

To the Editor:

In a recent letter (THIS JOURNAL, **32,** 338 (1955)) R. T. Sanderson gives two comments on a previous article (THIS JOURNAL, **32,** 141 (1955)). I should like to discuss his second comment from a high-school student's point of view.

If high-school chemistry were directed to those who do not plan to go to college, how would our demand for chemists be affected? I seriously doubt if it would help the present shortage. Teachers lacking thorough technical training could hardly be expected to attract others into the field they are teaching. As teachers of science, do you feel qualified to lead others into such foreign fields as law, athletics, etc.? The unqualified teacher without a sincere love for his subject cannot give an intimate explanation of the subject.

Such a course would touch mainly on the applications of chemistry. In an editorial (THIS JOURNAL, **32,** 1 (1955)) an excellent description is given of what is wrong with our present high-school teaching methods. Does Sanderson believe that his suggested courses taught by nonchemists will put emphasis upon science in the true sense of the word, or will they continue and perhaps further the emphasis upon the results of science?

I have tried to put into words the disadvantages of one of Sanderson's proposals in the eyes of a prospective fundamental chemist. When I referred to present high-school teaching methods my specific references were to my own high school, from which I have just graduated, and the many articles and letters in THIS JOURNAL concerning proposed solutions to high-school science teaching.

This letter has been my attempt to present a different approach, that of a student, to this problem.

TERRY COPELAND

PLAINVIEW, TEXAS

To the Editor:

In a recent article (THIS JOURNAL, **32,** 354 (1955)) a list of rules is given for the location of the decimal point in slide-rule calculations. I have been teaching the exponential system of finding the decimal point as described by F. Daniels ("Mathematical Preparation for Physical Chemistry," McGraw-Hill Book Co., Inc., New York, **1928,** Chapter I) for several years to freshman students with gratifying results. It would seem preferable to use a method which entails the use of a general principle rather than one which depends on memorization of rules which are soon forgotten.

A. G. PINKUS

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● AN INTRODUCTION TO INDUSTRIAL MYCOLOGY

George Smith, Lecturer in Biochemistry, London School of Hygiene and Tropical Medicine. Fourth edition. Edward Arnold Ltd., London, 1954. xiv + 378 pp. 161 figs. 15 × 22.5 cm. $6.

THIS is the fourth edition of Smith's deservedly popular general manual on fungi of importance in industry which first appeared more than a decade and a half ago.

As before, it is intended for those with little or no botanical knowledge, much less mycological training. It first orients the reader as to the place of the "moulds" in the plant kingdom, then proceeds to give, in simple language, details of the structure and reproduction of fungi essential to an understanding of them, together with their classification. New chapters on nomenclature and microscopy have been added. The main body of the book is concerned, as before, with an account of the groups of fungi of industrial importance. Several new genera have been added as have some 20 new photographs.

This new, expanded edition will prove of considerable value to those for whom it is intended, *i. e.*, the industrial man "faced for the first time with an industrial problem of 'mould' control," as Professor Harold Raistrick, who contributes a foreword, states it.

F. K. SPARROW

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ANN ARBOR, MICHIGAN

● INTRODUCTION TO THERMODYNAMICS OF IRREVERSIBLE PROCESSES

I. Prigogine, University of Brussels. Charles C. Thomas, Springfield, Illinois, 1955. ix + 115 pp. 14 × 22 cm. $4.75.

THIS book is the third on the same subject that has been reviewed for THIS JOURNAL by this reviewer. The first was by S. R. DeGroot (**29**, 51 (1952)); the second was by I. Prigogine and R. Defay (**32**, 341 (1955)). Because those two books were addressed to readers already expert in thermodynamics, the reviews did not mention obscurities and inconsistent terminology.

This book is different; it is supposed to be an introduction to the new ideas. In its preface the author states that the reader need not be fully acquainted with classical thermodynamics. Yet the author does not define fundamental terms like "heat" and "system." He is not clear in his treatment of spontaneous changes. From the book one obtains the idea that its author thinks that the expressions "spontaneous change" and "irreversible process" are identical in meaning.

The reaction of a mole of zinc with copper sulfate in water at 25° and one atmosphere is a spontaneous change. However, in the limit, it may be carried out in a cell by one method to yield maximum work. This method of carrying out the spontaneous change is called the reversible process for that change. All other methods of carrying out the same spontaneous change, in which less than the maximum work is realized, are called irreversible processes. The most irreversible process is the one in which the least work is obtained.

So apparently unaware is the author of these distinctions that even the title of his book is misleading. He is really discussing spontaneous changes.

The author's carelessness in defining what system he is talking about also causes the reader unnecessary difficulty. This carelessness is most objectionable in the crux of his argument, the discussion of entropy.

In this discussion the author makes a statement about entropy so contrary to accepted usage that one would think he ought to use some symbol other than S. On page 17, after dividing a "global system" into parts I and II (part I being inside a larger part II) he makes the postulate that the entropy change due to changes inside this system can never be negative in *either* part. (On the next page he says that eventually this central postulate of the book will have to be justified from statistical mechanics!) To realize how contrary to accepted usage the postulate is, one need only think of part I of the system as being a cell in which a spontaneous reaction is proceeding. The entropy change in part I is given by the equation:

$$\Delta S = \frac{q_r}{T}$$

It is clear that ΔS may be either positive or negative, depending on the sign of q_r. (It is the *sum* of the entropy changes in the two parts that is never negative.) Furthermore, if the entropy of part I is a property of that part of the system, such a property must be able to decrease as well as increase.

It is difficult to see how the results claimed by the proponents of the "thermodynamics of irreversible processes" can be obtained from equations resting on such shaky foundations. Possibly the answer is that the equations can be derived by other methods.

Although this reviewer noticed few, one obvious misprint occurs on page 6. The subscript on the second dn should be O_2, not C_2; the subscript on the third dn should be CO, not CO_2.

W. F. LUDER

NORTHEASTERN UNIVERSITY
BOSTON, MASSACHUSETTS

● INTRODUCTION TO THEORETICAL ORGANIC CHEMISTRY

P. H. Hermans, Director of the Institute for Cellulose Research, Utrecht. Edited and revised by *R. E. Reeves,* Research Consultant in Chemistry, Tulane University, and Chemist, U. S. Department of Agriculture. Elsevier Publishing Co., Inc., Houston, 1954. xii + 507 pp. 16 × 23.5 cm. $9.75.

THIS book is presented as an introduction to theoretical organic chemistry to bridge the gap between general organic textbooks and more advanced texts. It is apparently aimed at the college senior or beginning graduate student. The author has not attempted to present the subject in detail or to give a complete literature survey, but rather to introduce the whole broad panorama of physical organic chemistry. The uncommonly broad coverage, in which, perhaps, lies the greatest merit of this relatively small volume, is indicated by the following fields which are treated: quantum mechanics and structure theory, spectroscopy and other physical phenomena, equilibria and reaction kinetics, mechanisms of organic reactions and carbonium ion, carbanion, and free-radical intermediates. The product which results, however, is in many places rather superficial and in several places quite in error.

The author is most successful in presenting the physical aspects of organic chemistry. The student is immediately introduced to the concept of molecular models. The development of the resonance theory is well done despite several incorrect examples of its application; *e. g.*, tautomeric structures of pyrazole are described as resonance structures. The treatments of refraction, polarization, magnetic susceptibility, and other phenomena not usually included in introductory texts are clear and succinct.

The treatment of chemical reactions is conventional. Resonance structures are used in the interpretation of reaction mechanisms. This presentation, however, contains a number of errors of fact and/or interpretation which indicate that the author has lost pace with the subject. The reaction sequences proposed, for example, for ester condensation and for the base-catalyzed bromination of ketones are wrong in detail; lithium hydride (instead of lithium aluminum hydride) is described as a ketone-reducing agent.

Because of its scope this book should find a place particularly in the training of students still at an early stage. It should be used, however, only in conjunction with a course of lectures to fill in detail and to correct errors where required. The price is slightly high but not outrageous.

ANDREW STREITWIESER, JR.

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BERKELEY, CALIFORNIA

● MICHAEL TSWETT'S FIRST PAPER ON CHROMATOGRAPHY

G. Hesse and *H. Weil*. M. Woelm, Eschwege, Germany, 1954. 35 pp. 2 illustrations. 15 × 20.5 cm. Paper bound. $2.

THIS little brochure is divided into three parts: an English translation of Tswett's Russian paper: "On a New Category of Adsorption Phenomena and their Application to Biochemical Analysis," published in the Proceedings of the Warsaw Society of Natural Sciences for 1903 (18 pp.); notes on this paper by Hesse and Weil (4 pp.); and notes on Tswett's life (6 pp.). It contains a short bibliography and two photographs; a reproduction of Tswett's handwritten summary of his academic training and positions, and a snapshot of Tswett at the age of 40. The latter picture is from Dhéré's excellent biography of Tswett.

The translation, the original of which is not readily available, is noteworthy for many reasons. It shows that as early as 1903 Tswett had clear concepts about adsorption and its role in analysis, particularly in the extraction, separation, and recovery of the chloroplast pigments. It reveals that Tswett had already utilized his special columnar adsorption procedure and that he was aware of the importance of each step in this procedure; namely, the adsorption of a small amount of the mixture in a column of finely powdered sorbent forming a narrow initial zone of the sorbed substances, the resolution of these sorbed substances by washing with fresh solvent, and the recovery of the separated substances from successive portions of the percolate. It also discloses that Tswett had not yet proposed the now widely accepted "chromatographic methods" for this technique and "development of the chromatogram" for the washing of the sorbed substances with fresh solvent. It shows that Tswett had examined colorless substances with his method even though his subsequent terminology implied that the method was especially effective with colored substances.

The notes on Tswett's first publication are not nearly so clear as Tswett's own paper published 50 years earlier. Willstätter, for example, cannot be given credit for directing favorable attention to Tswett's work. Indeed, his criticism of Tswett's separation of several xanthophylls from leaves did much to discredit the chromatographic adsorption method. Ironically, Willstätter's contention that chromatographic adsorption produced additional altered pigments was prompted by the unobserved loss of several of these pigments in his own partition or fractionation procedure, a situation that was finally clarified by my own investigations of leaf xanthophylls in 1938.

In the notes it is misleading to claim that chromatography was taken up and extended by Willstätter's pupils. Actually the method was taken up and applied in chemistry by independent workers who had formerly been students of Willstätter. It is likewise deluding to consider the chromatographic procedure perfected by Tswett as equivalent to the columnar adsorption procedure employed earlier by petroleum chemists and by various analytical chemists. In most of these earlier columnar adsorption procedures there was no formation of the chromatogram with fresh solvent. And it is also incorrect to imply that Tswett did not realize the importance of this development, because he stressed it in 1903, and he proposed a special term "development of the chromatogram" for it in 1906.

The notes imply that Tswett employed the term "chromatography," but in most of his French, German, and Russian publications, Tswett commonly employed the adjective form of chromatography or "chromatographic." The noun and the verb forms were later widely adopted in English, probably without knowledge that these words had long been used with other meanings as indicated in my monograph on chromatographic adsorption analysis in 1942.

According to the notes on his life, Tswett was born in Italy of a Russian family then resident in Switzerland, and he remained a Russian subject from birth. Educated in Switzerland, Tswett felt like a foreigner when, at the age of 24, he obtained a position in Warsaw.

For the student of the history of chromatography, this booklet is an important contribution. But for those with time for only one of Tswett's papers, there should be greater interest in the 1906 paper in the *Berichte der deutschen botanischen Gesellschaft*, Volume 24, pp. 384–93 (1906). This paper contains a concise discussion of adsorption analysis and chromatographic methods. It also contains a careful description of the extensive resolution of chloroplast pigments by chromatography, and it introduces the terminology that is now widely accepted.

HAROLD H. STRAIN

ARGONNE NATIONAL LABORATORY
LEMONT, ILLINOIS

● RADIOISOTOPE CONFERENCE, 1954. VOLUMES I AND II

Edited by *J. E. Johnston*. Academic Press, Inc., New York, 1954. Volume I: xi + 418 pp. Figs. and tables. 16 × 25 cm. $10.80. Volume II: ix + 223 pp. Figs. and tables. 16 × 25 cm. $7.50. Price for two-volume set, $16.

THESE two volumes contain 70 technical papers presented at the second Isotope Conference held at Oxford in July, 1954. The conference was held to discuss and spread the knowledge of the application of radioisotopes. In selecting the papers for presentation emphasis was placed on "new ideas, new methods, and important new results."

In Volume I the papers are devoted to medical and physiological applications. The first 25 papers are included under the headings of therapy, diagnosis, and animal physiology and pathology. In the 15 papers on biochemistry, information is presented on chemical and biosynthesis of compounds as well as applications. Labeling and measurement techniques are described in detail in several of the papers. The remaining six papers are devoted to plant nutrition and allied subjects.

Volume II contains the papers in which the material is related to physical sciences and industrial applications. Preparation of radioactive gases and applications of numerous radioisotopes to the study of polymers, reaction mechanisms, exchange reactions, and catalytic poisoning are included in the eight papers in the field of chemistry. In the field of metallurgy there are three papers on segregation in metals, zone melting, and self-diffusion in binary alloys. Applications to physics and industrial applications are described in the remainder of the papers in Volume II.

Examples of the latter applications are measurement of deuterium by photoneutron production, determination of moisture by neutron scattering, gas and scintillation counting of carbon-14, measurement of thickness by alpha and gamma radiation, radiography, study of carbide cutting-tool life, static elimination, measurement of water flow in sewage purification plants, and use of a high-intensity gamma radiation source.

Both the printing and the paper are of excellent quality. There are very few typographical errors.

The two volumes definitely constitute a source of many new ideas, new methods, and new results not only in the rather well documented papers themselves but also in the interesting discussions following each paper. "Radioisotope Conference, 1954" should be valuable to those who are working in the wide variety of special fields covered, and should also appeal to those who have a general interest in recent developments in the applications of radioisotopes.

HERBERT M. CLARK

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● RECENT DEVELOPMENTS IN CELL PHYSIOLOGY

Proceedings of the Seventh Symposium of the Colston Research Society held in the University of Bristol, March 29–April 1, 1954. Edited by *J. A. Kitching,* University of Bristol. Academic Press, Inc., New York, 1954. ix + 206 pp. Many figs. 19.5 × 25.5 cm. $6.50.

As is pointed out in the preface to this volume, the term "cell physiology" is a very broad one. The organizers of this symposium seem to have used the title as an umbrella under which to shelter nearly any interesting topic which occurred to them. Of the 15 papers, four deal with various aspects of diffusion and transport across membranes, three with natural or experimental control of cell division, and the remaining eight represent scattered single hits on points lying in such areas as metabolic chemistry, embryology, protozoology, and morphogenesis. Such diversity may have made for an interesting meeting, but it appears to the reviewer that it detracts seriously from the value of the resulting volume. Rather than a book of clearly defined scope, bringing the experience and varied outlooks of workers from different disciplines to bear on an area of common interest, we have a series of individual and essentially unrelated papers collected under a title so broad as to be meaningless. Since it is unlikely to be indexed under eight or ten different headings, such a book seems destined to gather dust on the library shelf. Unless he is guided by an abstract or other citation to a specific chapter, who will look under the above title for a discussion of planarian regeneration or of synchronous division in *Paramecium?* Contrast the usefulness as a reference source of another recent British symposium volume bearing the stark title "Haemoglobin."

These considerations, of course, do not reflect on the quality of the individual papers; rather they suggest that some of them may not be as widely read as they deserve to be. The papers vary somewhat in length and in scope, some being mainly reports of original research while others have more of a review character. The only common factor amidst the diversity is the high quality of the presentations. It would appear that any physiologist or biochemist would find here several papers of considerable interest.

Review of 15 papers is clearly impossible, and a selection would reflect the reviewer's interests rather than any special excellence of the selected papers. It must suffice to repeat that the book contains a collection of individually interesting papers, but hardly a symposium.

DANIEL E. ATKINSON

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LOS ANGELES, CALIFORNIA

● TECHNIQUE OF ORGANIC CHEMISTRY. VOLUME VII: ORGANIC SOLVENTS

***J. A. Riddick* and *E. E. Toops, Jr.*, Commercial Solvents Corporation, Terre Haute, Indiana. Second edition. Interscience Publishers, Inc., New York, 1955. vii + 552 pp. 15.5 × 22.5 cm. $8.50.**

This is a timely revision and expansion of the well known work "Organic Solvents, Physical Properties and Methods of Purification," edited by Arnold Weissberger and Eric S. Proskauer. So many new and fancy solvents have appeared in chemical industry in recent years that the first edition has become out of date almost prematurely.

The authors remind us that "a wealth of new and accurate data has become available" in the field of evaluation of physical properties. Perusal of freezing-point values in this book, for example, suggests that publishers of standard chemical handbooks need to give their figures a thorough going over.

The section devoted to data tables classified by compounds shows substantial expansion in the revision. New kinds of data are included. For example, ethyl acetate occupies a whole page, as contrasted with a single line in an ordinary chemical handbook. Even 2-bromopropane, and *n*-butyraldehyde rate a half-page each of numerical data alone, not including expository information.

In addition to the property tables, each solvent, in proportion to its importance or diversity of uses, is discussed briefly as to source, and more extensively with respect to purification and handling. In the new edition data on toxicology have been added. Although most of us will not drink many of the solvents, considerable value will be found in the paragraphs on "maximum allowable concentration" of more or less toxic vapors, and this means practically all organic solvents. Wide use has been made of the high-class data on hydrocarbons available in recent years. An extensive bibliography is given. The problem of search for a special solvent is also facilitated by separate tables arranged not only in sequence by alphabet, but also by chemical principle, boiling point, freezing point, dielectric constant, and dipole moment.

This work will be an obvious purchase requirement for research laboratories in pure and applied chemistry, and particularly for the bookshelf of the chemical engineer. Even the teacher of organic chemistry will find the tabulations in numerical order useful for new problems and examination questions.

G. ROSS ROBERTSON

UNIVERSITY OF CALIFORNIA
LOS ANGELES, CALIFORNIA

● ANNUAL REVIEW OF NUCLEAR SCIENCE. VOLUME 4

Edited by *James G. Beckerley,* U. S. Atomic Energy Commission, *Martin D. Kamen,* Washington University Medical School, and *Leonard I. Schiff,* Stanford University. Annual Reviews, Inc., Stanford, California, 1954. x + 483 pp. 83 figs. 43 tables. 16 × 23 cm. $7.

Although the atom was once the province of the chemist, the nucleus appears to have been sacrificed to other disciplines. At least, I find that of the 17 chapters on various topics included in this volume, only a third are probably of immediate interest to the chemist. Most of the chapters are written by physicists at a level and point of view directed toward their co-workers. Some chapters serve, however, as stimulating and informative accounts for the general scientific reader as well as for the specialist. For example, the short chapter on Recent Developments in Proton Synchotrons impressed me with its casual narrative style in describing plans for accelerating particles up to 25 b. e. v.!

The more chemical topics include Fission Radiochemistry, Stable Isotopes as an Analytical Tool, Positronium, Biochemical Effects of Radiation, and Radioactivity in Geology and Cosmology. The chapter on analysis by isotope dilution is of classic

simplicity; the examples cited are problems in physics, but the methods will undoubtedly become standards for trace-element analysis. Chemists should find the chapter on positronium worth the price of admission. Not only is positronium the lightest atom, if not the simplest, but also the studies of its formation and decomposition in relation to molecular environment offer some basic chemical problems.

My general impression of this volume is one of diversity and heterogeneity. Only five topics are included this year which were covered last, and of these, three emphasize different subtopics. So practically all of the chapters cover several years' work rather than a single year. The subjects range from nuclear physics, fast electronics, and radiofrequency spectroscopy to analytical chemistry, biology, and cosmology. Six of the chapters are concerned primarily with experimental techniques while five are theoretical in nature. There are large variations in depth and manner of coverage; chapters range in length from 12 to 61 pages with 14 to 592 references. But the general quality of the reviews is high.

The wide range of topics reflects the extremely broad nature of nuclear science and suggests the magnitude of the editorial task. Also, it is apparent that only a modest fraction of each year's reviews will be of interest to any particular scientist. But I, for one, am very grateful that I do not have to depend entirely on the original literature where the signal to noise ratio is much less favorable.

H. S. GUTOWSKY

University of Illinois
Urbana, Illinois

● FROM CLASSICAL TO MODERN CHEMISTRY

A. J. Berry, **Fellow Emeritus of Downing College, Cambridge, England. Cambridge University Press, Cambridge, England, 1954. xii + 251 pp. 14.5 × 22.5 cm. $4.75.**

The purpose of the present work is primarily that of considering the historical development of certain branches of chemical science, which were either omitted from, or only adverted to in brief outline, in an earlier book, "Modern Chemistry—Some Sketches of Its Historical Development," published in 1946. The method of treatment, namely that of selecting particular topics and allocating them to separate chapters—that is, division according to subject matter and not according to periods of time—has again been adopted. After an opening chapter, Some Remarks on Theory in Chemistry, the subjects treated are: theory of heat; classical electricity and electrolysis; physical optics; molecular magnitudes; analytical chemistry; chemical formulas; valence, radicals, and constitution; kinetic chemistry. These form a somewhat disconnected series of essays, but each is filled with immense learning, and a unifying thread may be found in the author's insistence that the history of chemistry cannot be understood without attention also to the history of physics. All who are interested in the history of chemistry will want to read this book.

ANTHONY STANDEN

Interscience Encyclopedia, Inc.
Brooklyn, New York

● MECHANISM OF POLYMER REACTIONS

G. M. Burnett, **Professor of Chemistry, University of Birmingham, England. Interscience Publishers, Inc., New York, 1954. xv + 493 pp. Many figs. and tables. 16 × 23.5 cm. $11.**

This book constitutes Volume III of a series on high polymers, and is intended to replace the earlier work by Mark and Raff on high-polymer reactions published in 1941. Burnett's book is by no means a revision of the earlier work, since the field has advanced so rapidly in the past decade that an entire re-evaluation of the subject is required.

Burnett's book is an advanced text covering the entire field of polymer kinetics, and each subject is treated in a vigorous mathematical fashion followed by a summary of experimental results. Throughout, an extensive bibliography is provided. Although the author does not explicitly state that he presupposed some familiarity of the field on the part of the reader, nevertheless the level is such that this is required. The book should be useful to the specialist who wishes to supplement his knowledge obtained from textbooks on the field of high polymers and to obtain a review of the current status of the field of high-polymer reactions. This book is warmly recommended to all chemists engaged in the synthesis or degradation of high polymers. The general reader who has had advanced training in chemical kinetics may also find a perusal of this book rewarding.

GERALD OSTER

Polytechnic Institute of Brooklyn
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● PATENT LAW IN THE RESEARCH LABORATORY

John K. Wise. **Reinhold Publishing Corp., New York, 1955. 145 pp. 12 × 18 cm. $2.95.**

This small book is a timely discussion of invention, patents, and patent procedure in the light of the new (1953) patent act. Intending to give the industrial research worker a practical insight into the workings of the patent system, the author presents a readable and accurate account of the procedure from the conception of the invention to the issuance of the patent. Naturally for the research worker, the need for accurate and authenticated research records is stressed. Although the "Rules of Practice" are referred to in the book, it would have been helpful to tell the reader how he could secure this and other government publications pertaining to the Patent Office.

The author's style is so easy to read that the quoting of decisions at times seems stuffy—but then, the law is what the courts say it is. For a small book much is covered—topics particularly interesting in chemical cases, like the Markush type of claim.

This is a good book for the novice in patent matters as well as the oldster who wants to see how the new law has changed some of the features of patent law and practice. The decision that the deposition of a thesis in a university library is publication means a great deal to university research workers and should be understood by them.

KENNETH A. KOBE

University of Texas
Austin, Texas

● STRUCTURE OF MOLECULES AND INTERNAL ROTATION

San-Ichiro Mizushima, **Professor of Physical Chemistry, The University of Tokyo. Academic Press, Inc., New York, 1954. x + 244 pp. Figs. and tables. 16 × 23.5 cm. $6.**

The first 152 pages deal with a description of investigations on internal rotation. In the second part the theoretical aspects of such things as normal vibrations as well as experimental methods are treated. The book is written with the nonspecialist in mind. On page 58 the author quotes 0.5 kg.-cal. instead of five kg.-cal. as the resonance energy stabilizing substituted diphenyls. The very occasional quaint language complications do not detract from the interest of the book. One cannot help being impressed by the volume and significance of the studies of internal rotation. Why barriers are as high as they are still needs more detailed theoretical treatment. This is a book from one who is at home with his subject and should be read by all students in this field.

HENRY EYRING

University of Utah
Salt Lake City, Utah

● BIOCHEMISTRY OF THE AMINOSUGARS

P. W. Kent and M. W. Whitehouse, Department of Biochemistry, University of Oxford. Academic Press, Inc., New York, 1955. ix + 311 pp. 7 figs. 18 tables. 15 × 22 cm. $6.80.

In recent years knowledge of polysaccharides containing aminosugars and mucoproteins has expanded greatly. One has only to compare this volume with P. A. Levene's classical monograph on hexosamines and mucoproteins, published 30 years ago, to appreciate the advances that have been made in this area of biochemistry. A wide variety of mucopolysaccharides have been isolated in a fair degree of purity from animal tissues, and a beginning has been made toward an understanding of their physiological significance and how they are implicated in many pathological conditions.

It is not surprising, then, that the first half of this book is devoted to these macromolecules, the methods that have been employed in their isolation, and a description of the properties of aminopolysaccharides and mucoproteins. The authors suggest that the term "aminopolysaccharide" be used for those polysaccharides in which aminosugars account for all the nitrogen present. Such a nomenclature change should be adopted. The older terms, mucopolysaccharides and mucoproteins, frequently lead to confusion.

In this part of the book hyaluronic acid, heparin, chondroitin sulfate, chitin, mucosubstances of the digestive tract, and gonadotropic hormones are considered in detail from both the chemical and biochemical points of view. Other mucosubstances found in serum, bacteria, and fungi are described. Some of these yield bizarre products such as L-glucosamine from streptomycin, and 3-amino ribose from the antibiotic puromycin.

Analytical methods for the detection, isolation, and estimation of aminosugars are reviewed in the second half of the book. Experimental work relating to the structure and reactions of glucosamine, other aminosugars, and aminohexonic acids are treated in detail as well as methods for chemical synthesis of these substances and derivatives of them.

This book is very timely in view of the increasing attention that is being given to these materials as important factors in health and disease. It is highly recommended to those who desire a full discussion of the chemistry and biochemistry of aminosugars and their polymers.

F. A. CAJORI

University of Colorado
Denver, Colorado

● ORGANIC CHEMISTRY

Lewis F. Hatch, Professor of Chemistry, University of Texas. McGraw-Hill Book Co., Inc., New York, 1955. vii + 324 pp. 68 figs. 26 tables. 16 × 23.5 cm. $4.50.

Professor Hatch's "Organic Chemistry" is designed to accompany a terminal one-semester or one-quarter course for college students majoring in home economics, agriculture, and other subjects for which a brief but general acquaintance with organic chemistry is desirable. The depth and breadth of the author's treatment of the subject are such that his objectives are well achieved.

The fundamental facts of organic chemistry are presented via functional-group reactions in just about the proper detail to provide a reasonable background for the student, to be assimilable in the time available to the student, and to provide a working basis for understanding of the author's later topical chapters. Aliphatic and aromatic compounds are treated in a unified fashion, a technique which appears quite adequate for the author's intended level of sophistication.

Of the 20 chapters in the text, nine are devoted to the specific topics of Petroleum; Dyes; Proteins; Fats, Waxes and Detergents; Carbohydrates; Enzymes, Vitamins, Hormones and Antibiotics; Medicinals and Pharmaceuticals; Polymers; and Agricultural Organic Chemistry. In these chapters in particular, as well as in the remaining chapters in general, a laudable attempt has been made to emphasize the industrial, economic, and sociological aspects of the subjects without slighting the basic scientific side. The author's success in this attempt has been augmented by his emphasis on very recent developments in these practical aspects, as well as by the inclusion of numerous tables and illustrations adapted mainly from trade literature and company publications. Each chapter is followed by a list of suitable collateral reading sources and a set of 20 or so rather well chosen problems designed to emphasize both the scientific and practical aspects of the chapter topics.

Objections to the text are mainly minor ones. The author's brevity occasionally results in the use of undefined or poorly defined terms. Unbalanced equations and misleading statements are sometimes to be found, and a few more equations might have helped some of the verbal description. All in all, the number of objectionable features is very low, and the ones which were found did not appear serious from the student's point of view. The author's writing style is concise and clear with occasional flashes of humor. The text's typography, paper, and binding are excellent.

In general, Professor Hatch's book is quite well conceived and adequate for its intended purpose; it may be highly recommended.

WILLIAM A. BONNER

Stanford University
Stanford, California

● POMP AND PESTILENCE: INFECTIOUS DISEASE, ITS ORIGINS AND CONQUEST

Ronald Hare, Professor of Bacteriology, London University. Philosophical Library, Inc., New York, 1955. 224 pp. 13 × 20 cm. $5.75.

Open this book at random, and you will immediately become absorbed in these intriguing episodes from the history of medicine. The author begins with a chapter on the nature of infectious and contagious diseases and considers in the following chapter the origin of parasitism in prehistoric man and follows in succeeding chapters the spread of infection over the world. There are descriptions of the world's great epidemics of smallpox, bubonic plague, cholera, typhus, and influenza. Past beliefs about the nature and origins of diseases are revealed and the beginnings of quarantine systems as early as the fourteenth century are described. Finally, we come to modern science and its attack upon disease. From one point of view, Dr. Hare says the outlook is heartening, but from another point of view rather frightening, because as diseases are controlled, population rises only to die of malnutrition. Little has been written for the lay person concerning the origin of diseases; this, then, should be a popular book, for its subject matter is of universal interest.

GRETA OPPE

Ball High School
Galveston, Texas

● EPHRIAM'S INORGANIC CHEMISTRY

Edited by P. C. L. Thorne, Sometime Lecturer in Chemistry, Sir John Cass College, London, and Woolwich Polytechnic, and E. R. Roberts, Senior Lecturer in Chemistry, Imperial College of Science and Technology. Sixth edition. Interscience Publishers, Inc., New York, 1954. xii + 956 pp. 96 figs. Tables. 16.5 × 24.5 cm. $6.25.

This well-known book is an advanced textbook rather than a reference work. The present edition follows the same policies and arrangement as the earlier ones and so need not be reviewed in detail. By well chosen substitution of revised portions for obsolete ones it has been possible to keep this edition within 17 pages of the size of the last.

Out of the Editor's Basket

NEW APPARATUS & EQUIPMENT

▸ An aluminum block apparatus for determining existent gum in fuels by jet evaporation has been introduced by the Emil Greiner Company, 20–26 N. Moore St., New York 13, N. Y. This constant temperature bath is suitable for determining existent gum in aviation and motor gasoline using air preheated to a temperature of 320°F. or for jet fuels using steam as the vaporizing medium at a superheated steam temperature of 450°F.

▸ The new Vuscope, recently introduced by the National Instrument Co., converts any standard monocular microscope into a projection comparator with a built-in viewing screen. Contact the National Instrument Co., 2701 Rockwood Ave., Baltimore 15, Maryland, for information.

▸ Precision Scientific Co., 3737 W. Cortland St., Chicago 47, Illinois, has redesigned the "Micro-Set" Manostat to provide more accurate control of vacuums between atmospheric and 2-mm. absolute pressure.

A completely unitized apparatus with built-in leaks to the atmosphere and a pressure selection system, the Manostat also has a solenoid pressure controlling system, eliminating the need for surge tanks.

▸ Platinum resistance temperature detectors that are small and have high speed response now are offered for use in precision temperature measuring and control systems.

A product of Fielden Instrument Division of Robertshaw-Fulton Controls Co., 2920 N. Fourth St., Philadelphia 33, Pennsylvania. The unusually flexible detectors may be applied to temperature ranges from 330° to 1380°F.

▸ C. A. Brinkmann & Co., 378–80 Great Neck Rd., Great Neck, L. I., New York have available a "Laboratory News" illustrating their line of equipment along with some specialty instruments such as cameras, furnaces, etc., for scientific work.

▸ A high pressure valve with a micrometer stem has been developed and is manufactured by High Pressure Equipment Co., Inc., 1222 Linden St., Erie, Pennsylvania.

Perfect for bleeding and metering pressure letdown control, this Micro-Valve permits true micrometer control of all types of testing through the principle of differential screw threads. The slightest turn of the handle makes dial settings an easy-to-read record.

▸ A completely new hand-pump, all working parts made entirely of polyethylene is now being manufactured by Bel-Art Products, 4917 Murphy Place, West New York, New Jersey.

▸ With the growing need for drying small volumes of compressed gases to sub-zero dewpoints, Industrol Corporation, Roselle Park, New Jersey, announces the development of a completely new solid desiccant type Dynamic Dehumidifier.

▸ The Glo-Quartz Electric Heater Co., Inc., Willoughby, Ohio, is now presenting its line of new and exclusive "U" Type Quartz Immersion Heaters. This new electric radiant translucent fused quartz immersion heater was designed to solve the difficult problems encountered in the heating of acid electroplating and pickling solutions.

▸ Production of non-breakable polyethylene beakers and graduated cylinders is announced by the American Agile Corp., P. O. Box 168, Bedford, Ohio.

▸ The Bristol Co. of Waterbury 20, Connecticut, has just released a new Price List and Specification bulletin on their pH recorders and controllers for use with Beckman electrodes and amplifiers. Specifications are written to enable a user to select the pH indicating, recording, or automatically controlling equipment best suited to his particular needs.

▸ For laboratory convenience, the vacuum-distillation column introduced last year by Glenlab has been redesigned into a self-contained unit mounted in a metal shield. Facilities are provided for

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Tygon Tubing is not just translucent . . . it IS glass-clear, thus permitting instant visual inspection, more accurate flow control—better overall process control. Tygon is chemically inert, may be used anywhere for any liquid, gas or air transmission normally encountered in the laboratory. In addition it is extremely flexible and easy to handle, couples and uncouples quickly. Laboratory supply houses everywhere stock Tygon in all required sizes.
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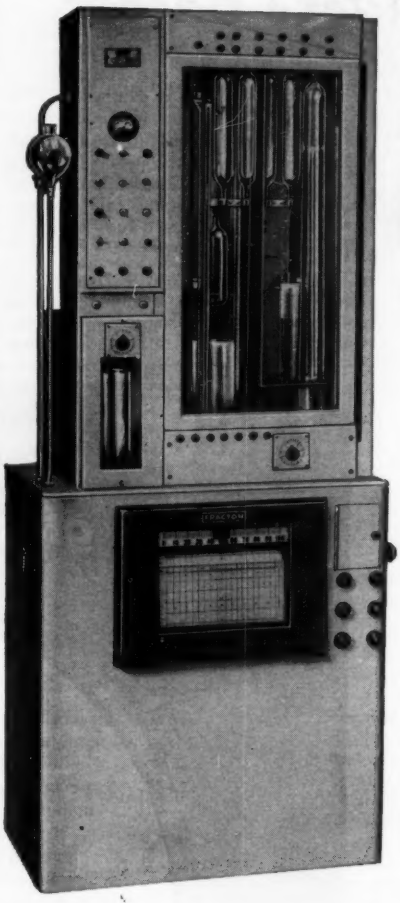

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rapid access to all parts requiring removal or adjustment during operation. The equipment, originally developed to coordinate with a standardization program relating to the use of ASTM-Type distillation for the characterization of lubricating oils and reduced crudes, is otherwise the same as that produced for Myers and Kiguchi of C. F. Braun and Co. For information contact the Glass Engineering Laboratories, 560 O'Neill Ave., Belmont, California

Automatic Titrator

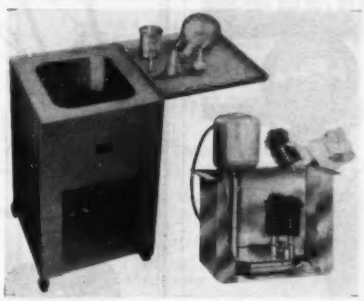
▸ The successful instrumentation of H. V. Malmstadt's second derivative method for potentiometric titration *Anal. Chem., 26,* 1348 (1954) has recently been announced by E. H. Sargent & Co., 4647 W. Foster Ave., Chicago 30, Illinois, and is said by that organization to promise a revolutionary improvement in automatic titrating techniques. It introduces the first basic

invention in the field since the earliest use of electrode potentials to determine equivalence points, employing the second derivative of the voltage/volume function both to determine the end point automatically and to actuate a burette valve automatically at that point.

Micro-Viewscope

▸ The Micro-Viewscope combines in one unit a microscope with built-in illuminating system and projection elements that render a brilliant image on the 8-in. viewing screen of the unit. Please write to William J. Hacker & Co., Inc., 82 Beaver St., New York 5, N. Y., for complete particulars.

Mobile Glassware Washer



▸ A new mobile laboratory glassware washer, reducing labor costs and eliminating glassware breakage, is announced by Labline, Inc., 3070 W. Grand Ave., Chicago 22, Illinois.

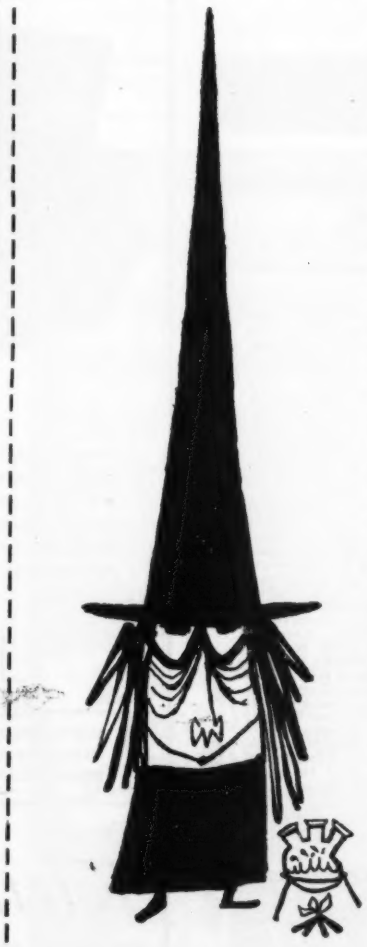
NEW LITERATURE

● A slide rule has now been devised that can give the liming requirements for any plant, flower, tree, shrub, vegetable, or farm crop grown in any type of soil. The plant group slide is positioned opposite the soil acidity reading and the amount of lime required for the best growing condition is read directly from the scale. Alum requirements for alkaline soils are also given. The rule has separate scales for small areas and for farm operations. A free brochure on the Soil Reaction Slide Rule is available from the LaMotte Chemical Products Company, Towson 4, Maryland.

● *Chemstrand—the fiber story,* is a well-illustrated booklet with samples of Acrilan, one of the products of Chemstrand Corp.,

(*Continued on page 37*)

WITCHCRAFT



or source without sorcery

Seems like witchery to some, but it's no dark secret that the people in our Special Apparatus Department are just fellows long on sleight of hand and experience when it comes to manipulating low-expansion glass.

Conjure up what you will in the way of tortured twists in tubes. Make a rough drawing of your most weird device. These fellows will stay with you, and you'll get what you want. It will be PYREX brand glass No. 7740, too. Lots of plotting went into it to give it high stability and low expansion.

For run-of-the-mill oddities, scan our brand-new catalog: "Custom Made Laboratory Glassware by Corning," 116 pages, listing 5,755 special pieces of glass. Not there? Send a sketch, we'll make it for you fast. The coupon will get you the catalog.

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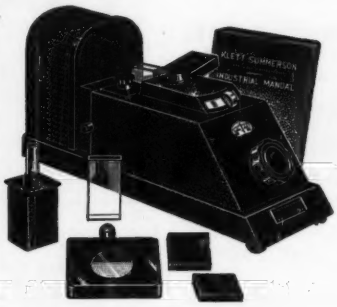
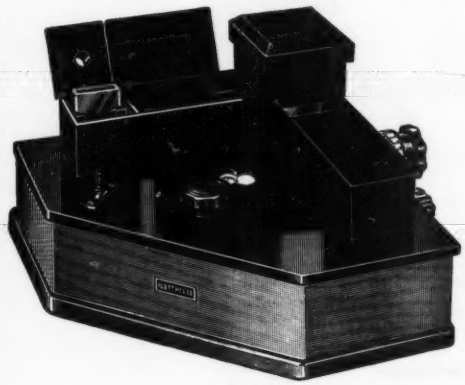


Photoelectric Glass Cell Colorimeter
No. 900-3

The Klett Fluorimeter



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Designed for the rapid and accurate determination of thiamin, riboflavin, and other substances which fluoresce in solution. The sensitivity and stability are such that it has been found particularly useful in determining very small amounts of these substances.

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Klett Manufacturing Co.
179 EAST 87TH STREET, NEW YORK N. Y.

(*Continued from page 35*)

and is now available from the Public Relations Dept. of Monsanto Chemical Co., St. Louis 4, Missouri.

● *The Story of the Ring-Jet Pump*, a new 8-page booklet just issued by F. J. Stokes Machine Co., 5500 Tabor Rd., Philadelphia 20, Pennsylvania, tells how and why the company developed its new line of diffusion and booster pumps to fill the need for faster pumping in the pressure range where most high vacuum processing is now being done.

● Precision Scientific Company, 3737 Courtland Ave., Chicago 47, Illinois, has published *Bulletin 240* as a reference manual for sanitary and public works engineers and chemists, public health officers, municipal officials, private industry, and local, state and federal agencies interested in the proper disposal of sewage and industrial wastes.

● *A New Recording Microbalance*, a publication by Axel H. Peterson, is available from the Mellon Institute, 4400 Fifth Ave., Pittsburgh 13, Pennsylvania.

● *Data Sheet No. 10.02a* gives specifications, dimensions, and operating characteristics of the Brown-Rubicon precision indicator. Now available in two over-all ranges, these instruments greatly speed laboratory-type electrical measurements. Contact Minneapolis-Honeywell Regulator Co., Wayne and Windrim Ave., Philadelphia 44, Pennsylvania.

● Testwork has eliminated the chance factor in both proposed and operating commercial ore dressing plants. Testing laboratories have been widely adopted by educational institutions, resulting in better trained engineers for industry. Denver Equipment Co., Box 5268, Denver 17, Colorado, has published a 76-page catalog, LG3-B10, *Denver Laboratory Equipment*, describing over 146 different items to help you establish your own laboratory testing needs.

● New *Bulletin No. 330*, recently released by the Burrell Corp. presents a new line of Castor Rheometers, Process Units, Gelometers, and auxiliary equipment, designed to meet the demand for better processing and control of the many dispersions, polymers and lubricants now being used by industry.

Copies are free on request to manufacturer: Burrell Corp., 2223 Fifth Ave., Pittsburgh 19, Pennsylvania.

● A brochure describing the 400 cycle Vernistat, and A.-C. potentiometer for use in servo systems and analogue computers, has been published by The Perkin-Elmer Corp., Norwalk, Connecticut.

● Process Chemical Specialties, Beverly, Massachusetts has just issued *Bulletin 1-54* on "TEAC-90" their Sequesterant, antioxidant, emulsion stabilizer.

● A twenty-eight page booklet covering *Motion Pictures Through the Microscope* has just been issued by Eastman Kodak Co.

(*Continued on page 38*)

The Welch **CATHETOMETER**

Rapid Leveling—Fine Adjustment—Graduations Engine Divided for Uniformity and Accuracy

- *Vertical range 100 cm*
- *Vernier reading to 0.05 mm*
- *Working distance 45 cm to infinity*
- *Magnification 12 x at 45 cm—8 x at infinity*
- *Level sensitive to 50 seconds*

This Cathetometer is intended for measurements and observations in both industrial and educational laboratories wherever an inexpensive instrument of good precision is needed. It is rigidly constructed and every essential adjustment can be made simply and positively.

The telescope is mounted horizontally on a carriage which may be moved up or down or around the 30-mm vertical rod. A tangent-screw adjustment permits precise leveling and a sensitive elevation adjustment is incorporated in the carriage. An auxiliary level in the base greatly accelerates the leveling process. Magnification is 12x at 45 cm., 8x at infinity.

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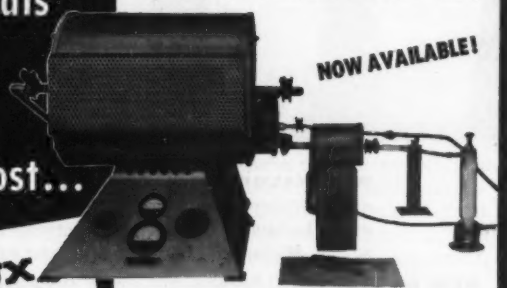
LEDOUX'S NEW HYDROGEN-DETERMINATOR determines hydrogen in Ti, Zr, V, W, Ce, Ta, Nb, Co and Ni metals and alloys as well as in many other metallurgical materials. The combustion technique is followed and accurate determinations are possible in concentrations ranging from 0.003% to those occurring in the metal hydrides. Reduces determination time to 20 minutes; so simple any technician can operate it; results are more accurate;



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can be used on widely differ[illegible]g metals and alloys; also effective in determining C and S; saves operating cost; priced lower than you think.

Ledoux's new HYDROGEN-DETERMINATOR was developed as a result of *Ledoux* & Co.'s continuous efforts to bring you newer and better methods and analytical instruments. For complete details—prices and literature—write to Dept. 15

LEDOUX & COMPANY

Teaneck, New Jersey

(*Continued from page 37*)

Prepared as a complimentary publication to the Kodak Data Book, *Photography Through the Microscope*, the new booklet has been published in answer to the request of many microscopists, and covers completely the additional technical problems involved in making motion pictures through the microscope. The latest methods are discussed in detail.

The booklet may be obtained without charge by writing Sales Service Division, Eastman Kodak Co., 343 State St., Rochester 4, New York.

● Bethlehem Apparatus Co., Inc., Hellertown, Pennsylvania, has issued a new catalogue, *No. 54*, on Laboratory Apparatus. One section is devoted to glassworking equipment and the other to mercury and its handling.

● A new 44-page illustrated catalog shows the complete line of laboratory equipment manufactured by Eberbach. Available free, this book features the firm's lab shakers, "Hollow Spindle" stirrers, electroanalyzers, slide cabinets and other apparatus. Request Catalog 55D from Eberbach Corporation, Ann Arbor, Michigan.

MISCELLANY

★ Vol. 27, No. 1, 1955, of "*Foote Prints*" has a very revealing article "Life With Lithium," which is available from the Foote Mineral Co., 18 West Chelten Avenue, Philadelphia 44, Pennsylvania.

★ Research and development chemists now can know that the same high purity chemicals they use in the laboratory also are available for full-scale commercial production. This is possible through a new system of bottle-cap identification inaugurated by the J. T. Baker Chemical Co. More than 200 of the Baker laboratory chemicals available in bulk carry a black and white cap seal on the top of the bottle stating "This Chemical Available in Bulk for Production Use."

★ The determination of cobalt according to Vogel (with ammonium thiocyanate and subsequent extraction of the blue complex with a water-immiscible solvent) is one of the oldest colorimetric tests. Unfortunately, some cobalt complexes ("Werner Compounds") do not respond to this. But they can be made to do so by evaporating the sample with H_2SO_4 into fumes, before taking up with water and applying the test. So say E. M. Goldstein and Leon Oberman of the Montclair Research Laboratories.

★ Vladimir Njegovan of Zagreb, Yugoslavia, suggests a simplified ammonia fountain consisting of two bottles, one inverted and resting on the mouth of the other. The upper bottle contains ammonia gas, and is provided with a one hole rubber stopper through which passes a 6-mm. glass tube extending into the lower bottle.

★ Acetonedicarboxylic acid, a well-known highly reactive chemical, was made available recently for the first time in pilot plant quantities by Chas. Pfizer & Co., Inc. A comprehensive data sheet and samples are available upon request from

(*Continued on page 41*)

an entirely new design

NALGENE HH POLYETHYLENE BEAKERS

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NEW NALGENE [HH] Beakers are made from entirely new molds, streamlined, tapered, with broad, sure-pouring spout . . . easier to handle, and nest compactly for convenience and space-saving. Ml capacity is marked permanently on each beaker.

NEW NALGENE [HH] Beakers are made from Super-Dylan* and have all the advantages of standard polyethylene beakers plus greater rigidity, greater tensile strength; a softening point over 250°F.; and improved chemical resistance especially toward solvents or concentrated detergents which often act as cracking agents on standard polyethylene.

Available in 30, 50, 100, 150, 250, 400, 600, and 1000 ml capacity. Prices from .60 to $3.85 each.

*Super-Dylan is the registered trademark of the Koppers Co.

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IMMEDIATE DELIVERY ON THESE ITEMS:

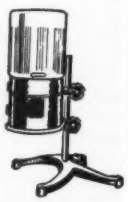
Hi-Speed Centrifuge

Rheostat controlled speeds 1800-5000 rpm suitable for micro and semi-micro analysis, and difficult chemical separations. Holds eight 15 ml straight or tapered tubes. Adapters for ½ to 5 ml tubes. Data sheet 204.

Heaters and Hot Plates

Built specifically for lab service. High quality porcelain refractory tops. Provisions for apparatus set-ups on heaters. Two adjustable heat types: Ful-Kontrol with autotransformer control from 0 to 750 watts and Type RH with built-in rheostat. Catalog 600.

Mag-Mix Stirrers



Magnetically agitate liquids under pressure, in vacuum. Mix viscous liquids. Stir batches of test tubes simultaneously. Rheostat controlled speed ranges. Two electric models, one air model for safe use with flammable liquids. Bulletins 590-R and 595.

Micro-Set Thermo-Regulators

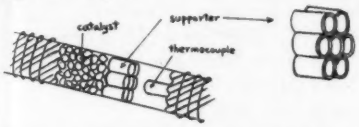
Control temperature within very narrow limits (models as sensitive as ±0.005°F). Operate electrical relay which controls heating elements, etc. Temperature setting may be pre-set or changed. Range spans as wide as —35° to +500°F. Bulletin 647A.

Precision Scientific Company
3731 West Cortland Street
Chicago 47

(*Continued from page 38*)

the company's Chemical Sales Division, 630 Flushing Ave., Brooklyn 6, New York.

★ Mr. Tsu Chia Shieh of the National Taiwan University, Taipei (Formosa) sends in the accompanying illustration of a "catalyst supporter," for use in vapor phase reactions. Pieces of Pyrex tubing are cut to appropriate lengths, held together by waterglass or some other binder, and inserted in the glass tubing containing the catalyst.



★ A new Norelco 40-minute, black and white, educational motion picture film with sound has been produced by the Research & Control Instruments Division, North American Philips Company, Inc., 750 S. Fulton Ave., Mount Vernon, New York. It may be booked on a loan basis or may be purchased at cost for school and industrial plant libraries.

Titled "The Ultimate Structure," the movie effectively employs audiovisual methods to explain a rather difficult and complex subject—X-Ray diffraction and spectrography. This documentary film is easily understood and it clearly outlines how elements and compounds are identified and measured through studies of the atomic structure.

★ *Critical Years Ahead in Science Teaching* is again available for distribution without cost through the kindness of the Carnegie Corporation. Copies may be obtained by writing: Mr. Elbert Weaver, Phillips Academy, Andover, Massachusetts. Self-addressed stickers for envelopes are appreciated.

★ *People, Products and Progress,* a film produced by the Chamber of Commerce of the United States predicts the life in 1975, as forecast by leading trade associations and business firms, and is available at 1615 H. St., N. W. Washington 6, D. C.

★ A continuous reactor for the preparation of organic chemicals, more versatile than any similar apparatus previously designed for laboratory use, has been developed in Kodak Research Laboratories.

The new type of reactor has important advantages over usual laboratory "batch process" equipment. It is simple and compact. Because it enables a given reaction to continue as long as starting materials are supplied and the end product removed, it offers possibilities for preparing considerable quantities of a desired compound.

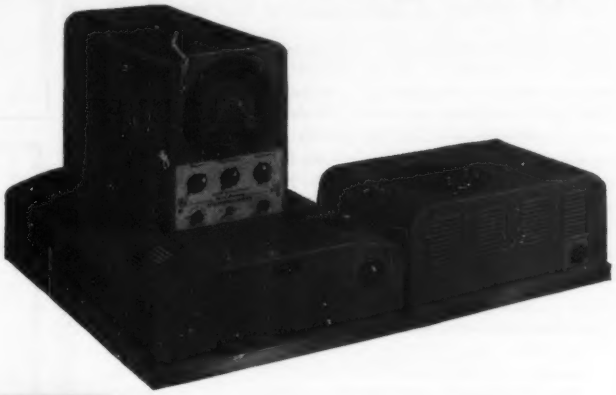
The reactor is relatively inexpensive. A laboratory-scale unit for a variety of reactions can be built of standard glassware and materials for less than $50.

★ Your hobby, preoccupation, or annoyance with terminology and nomenclature problems can help an important military project in the field of military engineering.

Ordnance engineering cuts across many fields of science and technology, and information for design work is drawn from many diverse fields of knowledge. If there is some chance that your subject

(*Continued on page 43*)

NEW LOWER PRICE
REMOTE INDICATING
SPECTROPHOTOMETER
PULSING ATTACHMENT



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RAPID SCANNING
SPECTROPHOTOMETER

Tooled to save costs. Now priced at $2396.00.
Reflection Attachment; $297.00.

The AO Rapid Scanning Spectrophotometer traces 60 separate curves per second recording a "moving picture" of color changes taking place in a specimen over the entire visible spectrum (wave lengths from 400 to 700 millimicrons). Allows fast analysis of transparent (up to 100mm thick) or opaque materials; gaseous, liquid or solid. In addition to general investigative work it can be used for following color changes and transient phenomena.

New Remote Indicating Spectrophotometer — The answer to certain control problems on flowing materials such as dyes or petroleum products. Indicator unit can be placed up to 50 feet away from spot where check on process takes place.

New Pulsing Attachment — This new electronic attachment allows a choice of one, six or sixty scans per second. Some slow chemical reactions cause the normal 60 cycle scan to produce partially overlapping or blurred spectrum curves. For studying such reactions, this attachment shows well separated, meaningful curves.

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☐ NEW AO Remote Indicating Spectrophotometer
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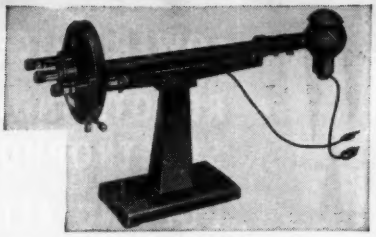

NEW

Lippich Type Polarimeter

(Schmidt & Haensch)

A precision instrument for measuring the rotation of the plane of polarization of all optically active substances. Big advantage is its glass circle instead of a metal circle. The scale on glass, instead of on metal, in conjunction with a micrometer plate, permits direct reading without vernier, resulting in greater speed and precision of reading. Glass circle is rigidly connected with the analyzer and carries two scales, an angular scale in degrees arc and a scale in international sugar degrees. Sodium vapor lamp is an integral part of the instrument and is always in alignment and ready for use.

Model A with receiving trough for tubes up to a length of 220 mm.
Model B with receiving trough for tubes up to a length of 400 mm.

Bulletin SH-344 on request

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(Continued from page 41)

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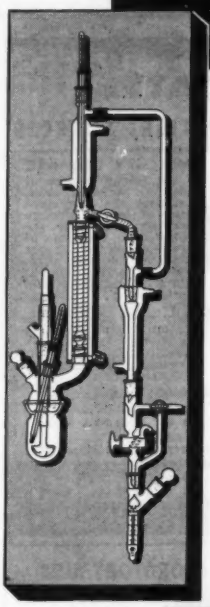

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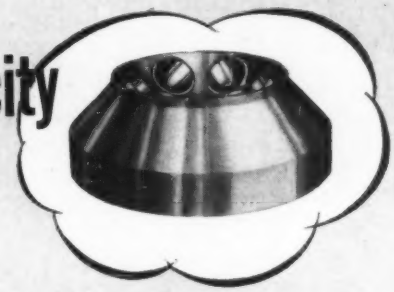

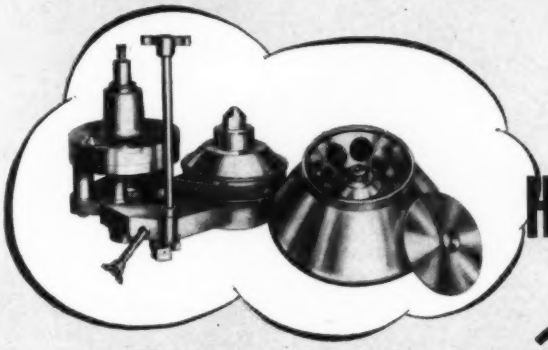

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